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(54) METAL SURFACE TREATMENTS, METHOD FOR TREATING METAL SURFACE, AND SURFACE-TREATED METALLIC MATERIAL

(57) Metal surface treatments in the form of an aqueous solution, aqueous dispersion or emulsion, which at least comprises an organic polymer having at least one group selected from among the nitrogen-bearing groups represented by general formula (a) and cationic sulfur-bearing groups or salts thereof. The treatments enhance the corrosion resistance in a non-coated state (resistance to blacking with boiling water in the case of aluminum DI cans), and improve the slipperiness (lubricity) of metal surfaces, the adhesion of a coating thereto and the corrosion resistance in a coated state. In formula (a), R_1 and R_2 are each hydrogen, hydroxyl, optionally substituted linear or branched C_1-C_{10} alkyl or optionally substituted linear or branched C_1-C_{10} alkanol residue or in formula (b), R_3, R_4 and R_5 are each hydrogen, hydroxyl, optionally substituted linear or branched C_1-C_{10} alkyl or optionally substituted linear or branched C_1-C_{10} alkanol residue.

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Description

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

The present invention relates to a metal surface treatment agent and method, and metallic materials treated with this agent, especially a metal surface treatment agent which improves corrosion resistance, sliding ability (lubricity), preservility of treated external appearance (stainability) and coating adhesion, a treatment method using the agent, and metallic materials treated with the agent.

Description of the Related Art

As a surface treatment of metallic materials such as coil coating of food cans, automobile bodies, steel plates, etc., conventional treatments using phosphate, chromate, non-chromate, etc. have been performed. For example, in the case of organic film coating of metal surface of iron, zinc, aluminum, etc. with paint, adhesive, etc., phosphate film is formed on the metal surface by the pretreatment with phosphate and the corrosion resistance and coating adhesiveness of the surface are improved by then forming organic coating film, such as paint, on that surface. However, metal surface treatment agents used in the conventional treatment methods, such as those with phosphate, do not sufficiently meet the recent demand for corrosion resistance, coating adhesiveness, and frictional resistance (also called sliding ability).

Therefore, in order to further improve corrosion resistance, a coating method has been employed wherein the phosphate-treated metal surface is treated with a primer coating agent prior to the final coating. However, the primer coating method has a problem that, although the corrosion resistance and coating adhesiveness of the surface are improved by this treatment, the overall procedure becomes complicated due to the additional coating process, and expensive.

As a metal surface treatment agent which aims at providing the surface with a high corrosion resistance and coating adhesiveness without primer coating, "a metal surface treatment agent for forming a complex conversion coating" has been proposed in Japanese Laid-open Publication No. Hei 5-117869. The metal surface treatment agent disclosed in said Japanese Laid-open Publication consists of a phosphate surface treatment aqueous solution containing one or more cationic nitrogen atoms and a cationic high molecular organic compound having a molecular weight 1,000 to 1,000,000 or its salt.

Also, Japanese Laid-open Publication No. Sho 51-73938 entitled "Surface Treating Method for Aluminum and its Alloy" proposes a surface treatment method for metal which aims at providing the metal surface with corrosion resistance and coating adhesiveness, especially limiting the metal to aluminum or the like. In this metal surface treating method is described a use of the treating solution comprising organic high molecular film-forming materials containing water-soluble resins such as vinyl acetate-vinilidene chloride, acrylic acid, etc. or emulsive resins and water-soluble titanium compounds as the main component.

Although, the metal surface treatment agents and solutions described above improve the corrosion resistance and coating adhesiveness of metal as compared with conventional metal surface treating agents, they still do not meet the recent required standard.

Especially, the conventional surface treatment agents mentioned above have problems that they are not suitable for preventing jamming in the case of fabricating food cans by shaping aluminum or its alloy, and do not providing metal surface with enough sliding ability in the case of coil-coating of steel plate.

Also, as for the metal surface treatment in more detail, for example, in the fabricating process of aluminum cans, the metal surface is removed of smut by treatment with acidic cleaner after the DI (drawing and ironing) process, further washed with water, and then subjected to the conversion coating process, etc. This conversion coating is performed in order to improve corrosion resistance, coating adhesiveness, and sliding ability of the metal surface. As described above, there are two conversion coating treatments, the chromate treatment and non-chromate treatment, the latter having recently become the main treatment from the standpoint of preventing environmental pollution. As a non-chromate conversion coating agent for this non-chromate treatment, the zirconium phosphate series, for example, is now widely used.

For example, in Japanese Laid-open Publication No. Sho 57-39314 entitled "Surface Treating Method for Aluminum", a method for treating aluminum surface with an acidic solution containing a zirconium salt, hydrogen peroxide, and phosphoric acid. Also, Japanese Laid-open Publication No. Hei 7-48677 entitled "Surface Treatment Solution and Method for both Aluminum DI Cans and Tin DI Cans" proposes a surface treatment method for aluminum DI cans using a surface treating solution for DI cans containing phosphate ions and zirconium compounds at pH 2.0 to 4.0, further an oxidizing agent of less than 500 ppm and hydrofluoric acid or at least one kind of fluorides of less than 2000 ppm.

Usually, in the fabricating process, aluminum cans are thoroughly washed with water after the conversion treatment, drained, dried in open air, and then subjected to printing and painting. At the time of proceeding to the printing

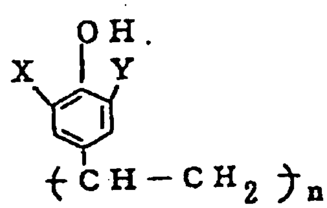
and painting process, the width of the belt conveyer for transporting aluminum cans suddenly narrows. At this time, there is a possibility of jamming due to contact among the cans and with the conveyer guide, leading to the reduced conveying speed and production efficiency of cans.

In general, by treatment with agents of said zirconium phosphate series, coating films of zirconium oxide and zirconium phosphate are formed on the aluminum surface, causing the aggregation destruction when the thickness of these films exceeds a certain limit, often resulting in the inferior coating adhesiveness of the surface. Furthermore, said inorganic coating film is inferior in the surface sliding ability, often causing the jamming during the transportation of cans over the belt conveyer and leading to the reduction of production efficiency of cans as described above.

Therefore, recently, a surface treatment agent to form not only inorganic but also organic coating film has been proposed. For example, Japanese Laid-open Publication No. Hei 7-331276 entitled "Surface Treating Composition and Method for Metallic Materials Containing Aluminum" proposes a surface treating composition containing phosphate ions, water-soluble zirconium compounds, fluorides and a water-soluble polyamide having at least one selected from tertiary amines and polyalkyl glycol groups.

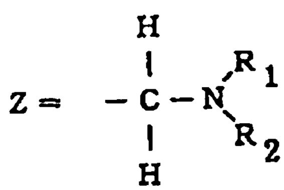
However, when the thickness of zirconium phosphate coating film formed from the water-soluble zirconium compounds contained in the surface treatment composition described in said Japanese Laid-open Publication exceeds a certain limit, it causes the aggregation destruction of films, resulting in the reduction of coating adhesiveness.

Therefore, a surface treatment agent has been proposed which forms only an organic coating film, without forming an inorganic coating film. For example, Japanese Laid-open Publication No. Hei 4-66671 entitled "Surface Treatment Solution for Aluminum and Aluminum Alloy" describes a surface treatment solution containing phosphate ions at 1/30 g/l, condensed phosphate ions at 0.1~10 g/l, and a water-soluble resin represented by the following formula (1) at 0.1~20 g/l as the solid component with a pH value of 2.0~6.5.



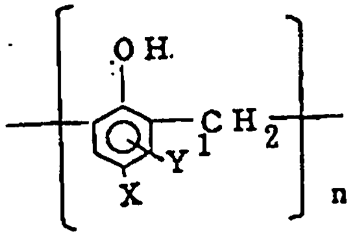
Formula (1)

(where n = 10~80, X and Y = H or Z represented by the following formula

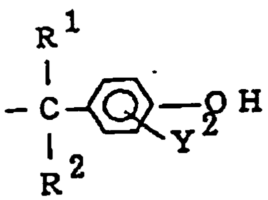


R_1 and R_2 = C_1~ C_{10} alkyl group or hydroxyalkyl groups, and the substitution ratio of Z per aromatic ring is 30~ 200 mole percent.)

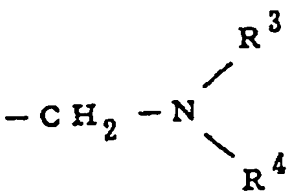
Also, Japanese Laid-open Publication No. Hei 7-278410 entitled "Surface Treatment Polymer Composition for Metallic Material and Treatment Method using the Same" proposes a surface treatment agent which forms an organic coating film of phenolic resin in addition to an inorganic coating film. That is, this treatment agent contains an acidic compound and a polymer represented by the following formula (2) (where X = H, C_{1-5} alkyl or C_{1-5} hydroxyalkyl group, groups represented by the following formula (3), etc., R^1, R^2 = H, OH, C_{1-10} alkyl and C_{1-10} hydroxyalkyl groups, etc., Y^1, Y^2 = H or Z group represented by the following formulae (4) or (5), R^3~R^7 = C_{1-10} alkyl, C_{1-10} hydroxyalkyl groups, etc., the average number of substituted Z groups in each benzene ring of the polymer molecules = 0.2~1. 0, n = 2~50). In this document, a metal surface treatment method using said agent at pH 2.0~6.5.



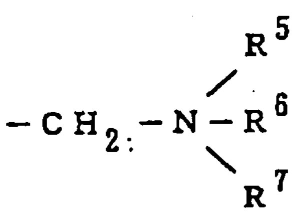
Formula (2)



Formula (3)

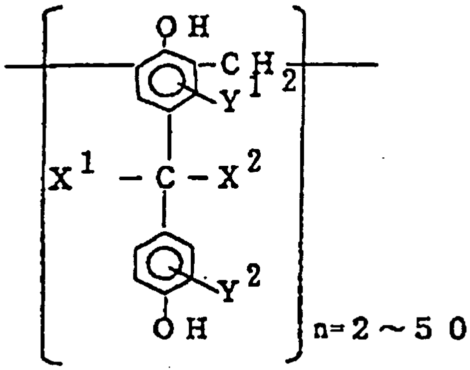


Formula (4)

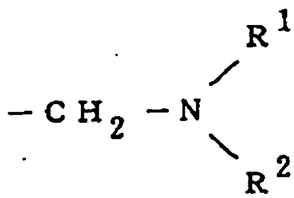


Formula (5)

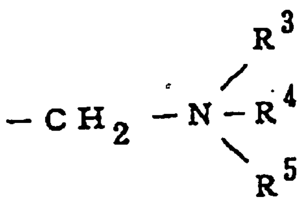
Also, Japanese Laid-open Publication No. Hei 7-278836 entitled "Surface Treatment Composition and Method for Aluminum-containing Metallic Materials" proposes a treatment agent which forms an organic coating film of bisphenol A resin, in addition to an inorganic coating film. That is, this agent contains phosphate ions, condensed phosphate ions and aqueous polymer in the weight ratio of 1~30 : 0.1~10 : 0.2~20, and contacts said metal surface at 30~65°C for 5~60 seconds, which is then washed with water and heat-dried. Said water-soluble polymer has the chemical structure represented by the following formula 6, where Y^1 and Y^2 are H atoms or Z group represented by the following chemical formulae (7) or (8), and the average substitution number of Z group on the benzene ring in the polymer molecule is 0.2~1.0.



Formula (6)



Formula (7)



Formula (8)

However, all surface treatment agents disclosed in Japanese Laid-open Publication No. Hei 4-66671, Hei 7-278410 and Hei 7-278836 have a problem that, unless an organic coating film layer with the thickness exceeding a certain limit is formed with said agent, the corrosion resistance of the metal surface prior to coating is insufficient. There is also a problem that, when the organic coating film becomes too thick, it generates the interference color derived from the organic polymer compounds, resulting in inferior external surface appearance.

SUMMARY OF THE INVENTION

This invention is conceived to overcome the above described problem, and provides a metal surface treatment agent and method which will improve not only the corrosion resistance prior to coating (blackening resistance in boiling water in the case of aluminum DI cans), but also the sliding ability, coating adhesiveness, preservility of treated external appearance (stainability), and corrosion resistance after coating, and metallic materials surface-treated with the agent and having these properties.

An organic high molecular compound or its salt contained in the metal surface treatment agent in accordance with the present invention is, for example, either water-soluble, water-dispersive or emulsive high molecular compound or its salt, containing at least more than one nitrogen atom. Preferably, the high molecular compound is a compound having one or more than two kinds of resin skeletons derived from epoxy resin, acrylic resin, phenolic resin, urethane resin, polybutadiene resin, polyamide resin, and olefine resin. More preferably, at least one of the nitrogen atoms in the organic high molecular compound has the structure represented by the chemical formulae (9) or (10).

$$-\mathrm{N}\begin{array}{l} \diagup\, R_1 \\ \diagdown\, R_2 \end{array} \qquad \text{Formula (9)}$$

(where R_1 and R_2 = H, OH or $C_{1\sim10}$ straight or branched chain alkyl groups with possible substitutions, or $C_{1\sim10}$ straight or branched chain alkanol groups with possible substitutions)

$$-\overset{+}{\mathrm{N}}\begin{array}{l} \diagup\, R_3 \\ -\,R_4 \\ \diagdown\, R_5 \end{array} \qquad \text{Formula (10)}$$

(where R_3, R_4 and R_5 = H, OH or $C_{1\sim10}$ straight or branched alkyl groups with possible substitutions, or $C_{1\sim10}$ alkanol groups with possible substitutions)

Also preferably, at least one of the nitrogen atoms in the organic high molecular compound has the structure represented by any one of the following chemical formula (11).

$$-\mathrm{N}\begin{array}{l} \diagup\, CH_3 \\ \diagdown\, CH_3 \end{array}, \quad -\mathrm{N}\begin{array}{l} \diagup\, CH_2CH_2OH \\ \diagdown\, CH_3 \end{array}, \quad -\mathrm{N}\begin{array}{l} \diagup\, CH_2CH_2OH \\ \diagdown\, H \end{array} \qquad \text{Formula (11)}$$

Salts of the organic high molecular compounds are exemplified by those of alkali metals such as sodium, potassium, etc., alkali earth metals such as calcium, magnesium, etc., and ammonium salts.

Also, the molecular weight of the organic high molecular compound or its salt in accordance with the present invention is preferably 300~10,000. When the molecular weight is less than 300, corrosion resistance and friction resistance (called sliding ability hereafter) are inferior. On the other hand, when the molecular weight exceeds 10,000, water-solubility is inferior.

The concentration of the organic high molecular compound or its salt in the metal surface treatment composition in accordance with the present invention is preferably 0.01~10 g/l, and more preferably 0.1~5 g/l. When the concentration is less than 0.01 g/l, the organic high molecular compound or its salt cannot exert their binder effect, resulting in the inferior physical durability of undercoating film. On the other hand, the concentration exceeding 10 g/l results in the inferior corrosion resistance.

The organic high molecular compound of the present invention more preferably contains 1~5 phenyl groups, 1~5 hydroxyl groups and 1~10 nitrogen atoms per 500 molecular weight. With less than one phenyl group per 500 molecular weight, corrosion resistance and sliding ability become inferior. With more than 5 phenyl groups per 500 molecular

weight, water-solubility, corrosion resistance and coating adhesiveness become inferior. Also with less than one hydroxyl group per 500 molecular weight, coating adhesiveness and water-solubility of the compound in the metal surface treatment solution become inferior. On the other hand, with more than 5 hydroxyl groups per 500 molecular weight, corrosion resistance and sliding ability also become inferior. Furthermore, with less than one nitrogen atom per 500 molecular weight, coating adhesiveness of the compound and its water-solubility in the metal surface treatment solution become inferior. On the other hand, when there are more than 10 nitrogen atoms per molecular weight 500, corrosion resistance becomes inferior.

Nitrogen containing organic high molecular compounds in accordance with the present invention are preferably copolymers of the following monomers when they have, for example, the skeleton of acrylic resin. That is, (a) the nitrogen-containing acrylic monomer is exemplified by $C_{1\sim5}$ (meth)acrylamide, dimethylacrylamide, N-methylolacrylamide, N-methylaminoalkyl(meth)acrylamide, N-dimethylaminoalkyl(meth)acrylamide, N-methylalkyl(meth)acrylamide, N-methylolaminoalkyl(meth)acrylamide, N-trimethylaminoalkyl(meth)acrylamide, etc.

Also, (b) the hydroxyl group containing acrylic monomer is exemplified by $C_{1\sim5}$ hydroxyalkyl(meth)acrylate and alkylacrylate.

Furthermore, instead of jointly using said (a) nitrogen-containing and (b) hydroxyl group containing acrylic monomers, a nitrogen and hydroxyl group containing acrylic monomer such as hydroxyalkylmethyl(meth)acrylamide, etc. may be used.

(c) Phenyl group containing monomers are exemplified by styrene, t-butylstyrene, vinylphenol, vinyltoluene, benzyl(meth)acrylate and their halogen derivatives.
(d) Additional acryl monomers may be exemplified by acrylic acid, methacrylic acid $C_{1\sim5}$, alkyl(meth)acrylate, isobornyl(meth)acrylate, etc.

Copolymerization ratios of copolymers composed of monomers described above are preferably 5~60 weight percent for nitrogen-containing acrylic monomers (a), 20~80 weight percent for hydroxyl group containing acrylic monomers (b), 5~50 weight percent for phenyl group containing monomers (c), and 30 or less weight percent for other acrylic monomers (d). More preferably, these copolymerization ratios are 10~40 weight percent for nitrogen-containing acrylic monomers, 40~70 weight percent for hydroxyl group-containing acrylic monomers, and 10~30 weight percent for phenyl group-containing monomers.

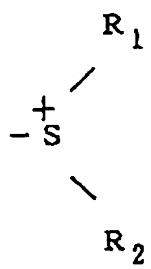
Furthermore, in the preferred embodiments of the present invention, the copolymerization ratios described are the mixing weight ratios of monomers at the time of copolymer production assuming that copolymers are generated according to said mixing weight ratios.

When the copolymerization ratio of nitrogen-containing acrylic monomer in said copolymer is less than 5 weight percent, nitrogen atoms at the copolymerization site of said monomer cannot be sufficiently coordinated to the metal surface, resulting in decreased coating adhesiveness. On the other hand, when the ratio exceeds 60 weight percent, adhesiveness of undercoating film itself to the metal surface becomes inferior. Also, when the copolymerization ratio of hydroxyl group-containing acrylic monomer in said copolymer is less than 20 weight percent, coating adhesiveness becomes inferior. On the other hand, when the ratio exceeds 80 weight percent, corrosion resistance is inferior. Furthermore, when the copolymerization ratio of phenyl group-containing monomer in said copolymer is less than 5 weight percent, sliding ability and blackening resistance in boiling water are inferior. On the other hand, when said ratio exceeds 50 weight percent, water-solubility and coating adhesiveness are inferior. As used here, "blackening resistance in boiling water" refers to the resistance of surfaces (aluminum) food can, prior to coating against blackening in boiling tap water or the like for sterilization due to the reaction of the surface prior coating with metals in water.

Organic high molecular compounds or their salts containing cationic sulfur atoms in accordance with the present invention are, for example, either water-soluble, water-dispersive or emulsive resins, or their salts. Preferably, they are compounds wherein the cationic sulfur atom-containing resin has one or more than two kinds of resin skeletons derived from epoxy resin, acrylic resin, urethane resin, polybutadiene resin, polyamide resin, phenolic resin and olefine resin.

Resin skeletons described above can provide coating films on the metal surface with additional corrosion resistance.

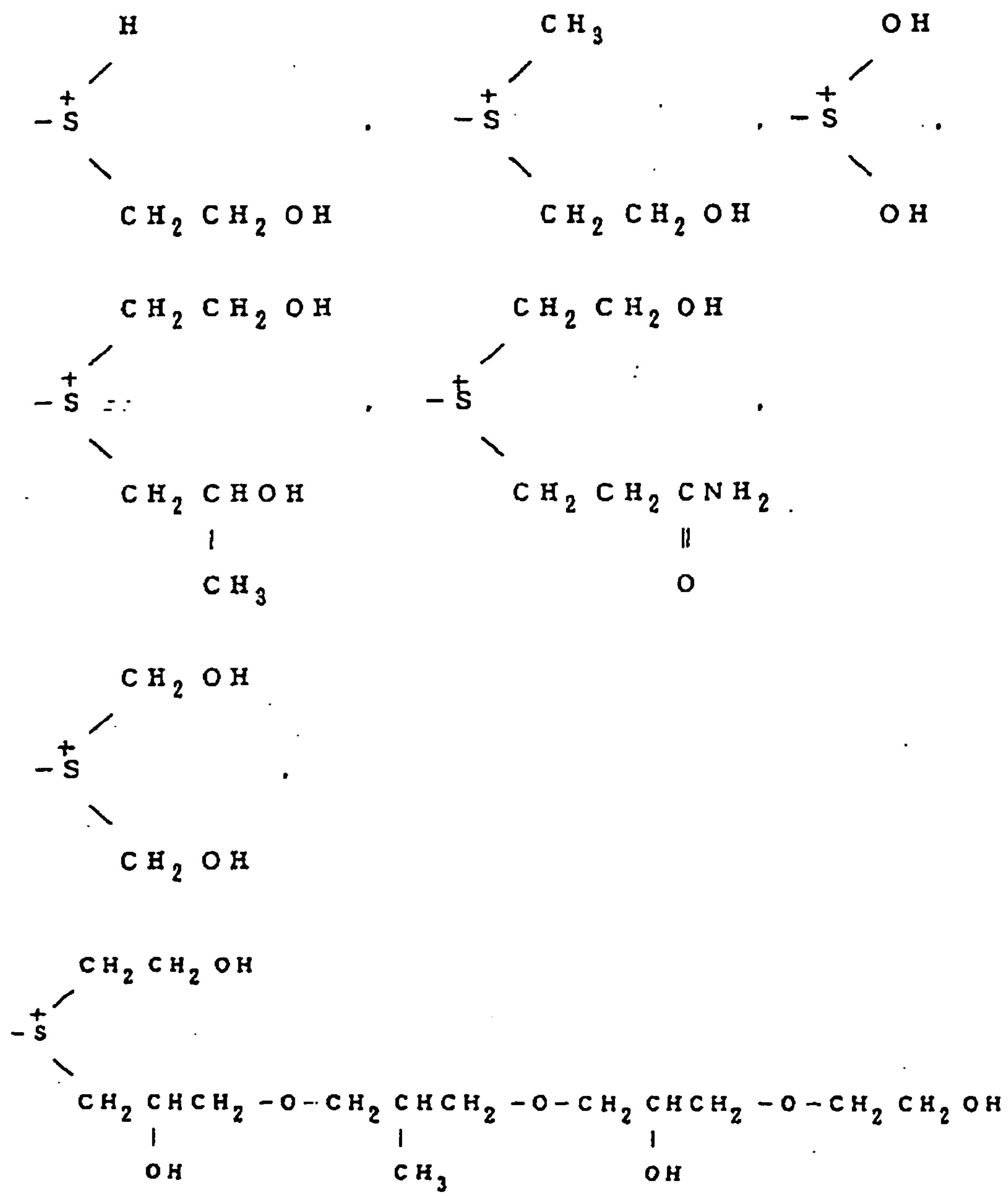
For example, at least one of the cationic sulfur atom-containing resins or their salts has the structure represented by the chemical formula (12).



Formula (12)

(where R_1 and R_2 = H, OH or $C_{1\sim15}$ straight or branched chain alkyl groups with possible substitutions or $C_{1\sim15}$ straight or branched chain alkanol groups with possible substitutions)

Most preferably, at least one of the sulfur atoms in the cationic sulfur atom-containing resin has any one of the following structures.



With the cationic sulfur atom-containing resin described above, the coordinating amount of resin to the metal increases, resulting in improved corrosion resistance and sliding ability.

Also, salts of the cationic sulfur atom-containing resin include those of alkali metals such as sodium, potassium, etc., alkali earth metals such as calcium, magnesium, etc., ammonium salt, etc.

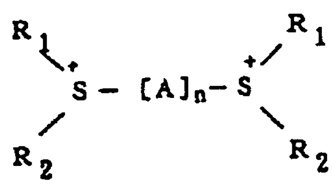
In addition, the molecular weight of the cationic sulfur atom-containing resin in accordance with the present invention is preferably 1,000~10,000. When the molecular weight is less than 1,000, corrosion resistance and sliding ability

are inferior. On the other hand, when the molecular weight exceeds 10,000, water-solubility becomes inferior.

Furthermore, the concentration of the cationic sulfur atom-containing resin and its salt in the metal surface treatment composition of the present invention is preferably 0.01~10 g/l, and more preferably 0.1~5 g/l. When the concentration of the cationic sulfur atom-containing resin and its salt is less than 0.01 g/l, they cannot exert their binder effects, resulting in the inferior physical durability of the undercoating film. On the other hand, when the concentration of the cationic sulfur atom-containing resin and its salt exceeds 10 g/l, the corrosion resistance becomes inferior.

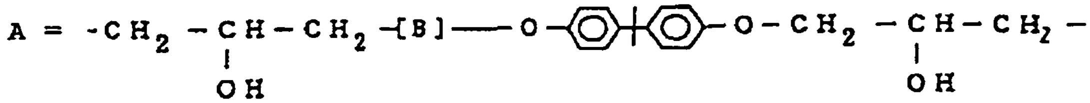
The cationic sulfur atom-containing resin in accordance with the present invention preferably contains 1~5 phenyl groups, 1~12 hydroxyl groups and 0.1~7 sulfur atoms per molecular weight 500. With less than 1 phenyl group per molecular weight 500, the corrosion resistance and sliding ability are inferior. On the other hand, with phenyl groups exceeding 5 per molecular weight 500, the water-solubility and coating adhesiveness become inferior. Also, with less than 1 hydroxyl group per molecular weight 500, coating adhesiveness and water-solubility into the metal surface treatment solution become inferior. On the other hand, with more than 12 hydroxyl groups per molecular weight 500, the corrosion resistance and sliding ability are inferior. Furthermore, when the number of the cationic sulfur atoms is less than 0.1 per molecular weight 500, the coating adhesiveness and water-solubility into the metal surface treatment solution are inferior. On the other hand, when the number of the cationic sulfur atoms exceeds 7 per molecular weight 500, the corrosion resistance is inferior.

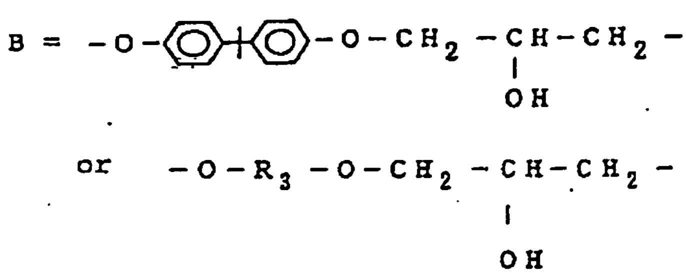
Examples of cationic sulfur atom-containing resins which meet the conditions (criteria) described above are shown in the following chemical formulae (13)~(17).



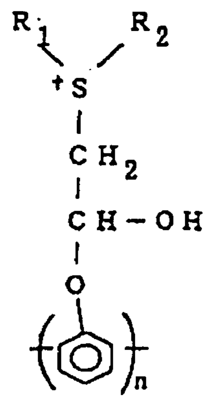
Formula (13)

(where,



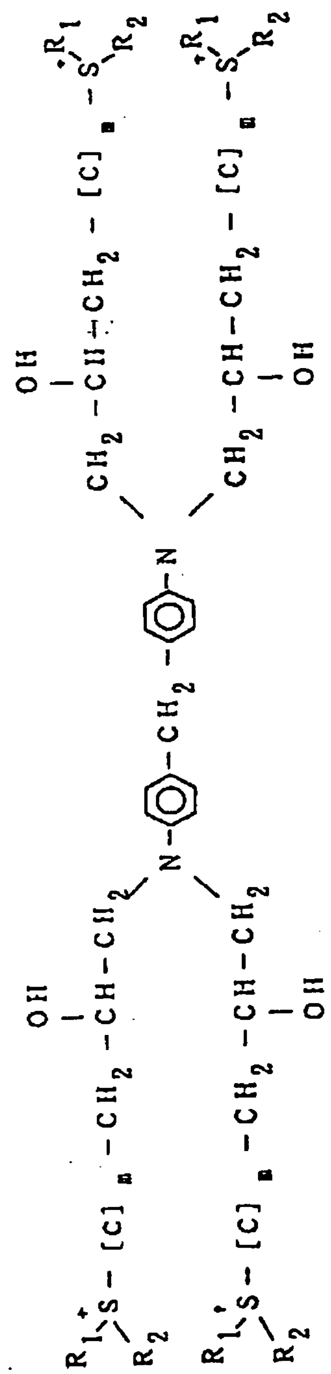


R_1 and R_2 = H, OH or $C_{1\sim15}$ straight or branched chain alkyl groups with possible substitutions, or $C_{1\sim15}$ straight or branched chain alkanol groups with possible substitutions, R_3 = $C_{10\sim18}$ straight or branched chain alkyl groups)



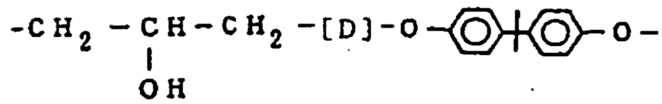
Formula (14)

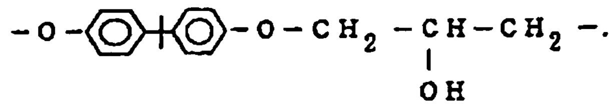
(where R_1 and R_2 = H, OH or $C_{1\sim15}$ straight or branched chain alkyl groups, or $C_{1\sim15}$ straight or branched chain alkanol groups with possible substitutions)



Formula (15)

(where

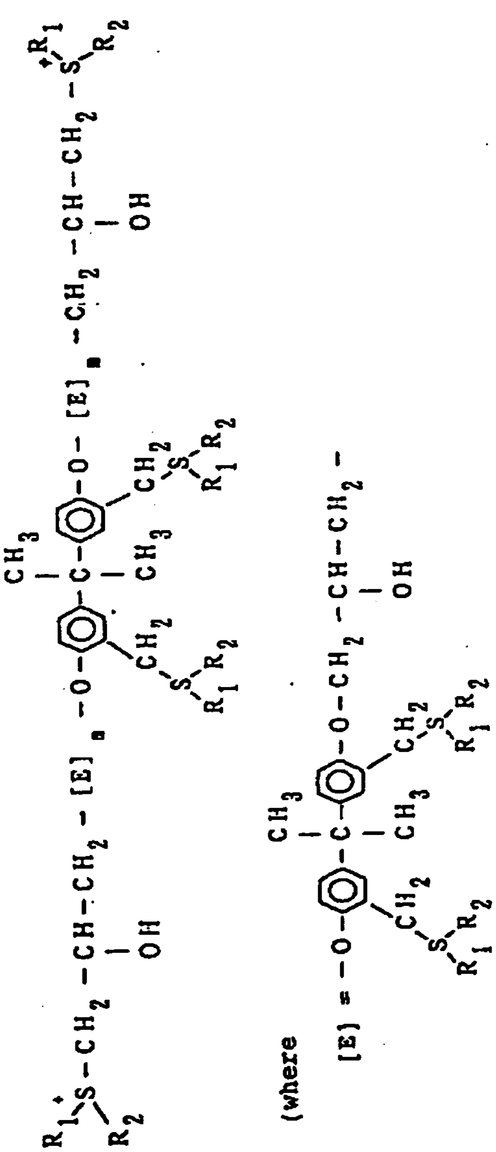
[C] = 

[D] = 

or $-O-R_3-O-CH_2-\underset{\displaystyle OH}{\underset{|}{C}H}-CH_2-$

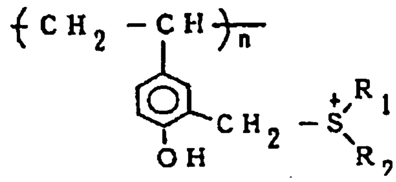
R_1 and R_2 = H, OH or $C_{1\sim15}$ straight or branched chain alkyl groups with possible substitutions or $C_{1\sim15}$ alkanol groups with possible substitutions,
R_3 = $C_{10\sim18}$ straight or branched chain alkyl groups)

Formula (16)



R_1 and R_2 = H, OH or $C_{1\sim15}$ straight or branched chain alkyl groups, or $C_{1\sim15}$ alkanol groups with possible substi-

tutions)

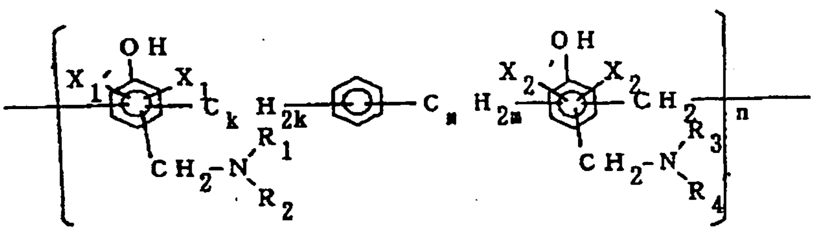


Formula (17)

(where R_1 and R_2 = H, OH or $C_{1\sim15}$ straight or branched chain alkyl groups, or $C_{1\sim15}$ alkanol groups with possible substitutions)

The presence of hydroxyl groups in the compounds having the chemical formulae (13)~(17) improves the coating adhesiveness of film. Also, blackening resistance in boiling water and sliding ability of films are improved, depending on the position of phenyl group in the compounds having the chemical formula (13). Furthermore, by the sulfur atom in the compound having the chemical formula (13), the adhesiveness of film to metal is improved. In addition, ionization of sulfur atom in compounds having the chemical formula 13 contributes to the stability of the treatment bath. Here, by blackening resistance in boiling water is meant blackening phenomena of surface of food cans (aluminum) prior to coating by the treatment in boiling tap water or the like for sterilization.

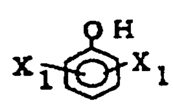
In the following are described nitrogen-containing organic high molecular compounds in accordance with the present invention. One example of phenolic resin consists of the repeating structuring units having the following chemical



Formula (18)

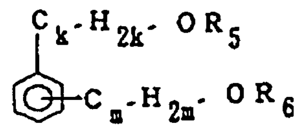
(where R_1, R_2, R_3 and R_4 = H or $C_{1\sim5}$ substituted and unsubstituted alkyl or alkanol groups; X_1, X_1', X_2 and X_2' = H, OH or $C_{1\sim5}$ substituted and unsubstituted alkyl groups; and k and m = 1~5; n = 1~3)

The phenolic resin described above is obtained by reacting a phenol having the following chemical formula (19) (1 mol) with a dialkylbenzene glycol having the chemical formula (20) (0.02~0.6 mol) and formaldehyde the amount of which is such that the sum of formaldehyde and said dialkylbenzene glycol is adjusted to be 0.7~0.9 mol in the presence of an organic or inorganic acid as the catalyst, and further reacting the resultant phenolic condensation product with amines having the following chemical formula (21) (0.5~2.0 mol) and the equimolar amount of formaldehyde (the aminomethylation according to Mannich reaction).



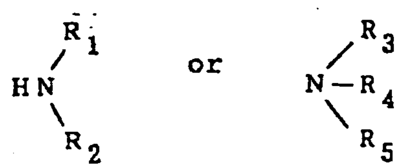
Formula (19)

(where X_1, X_1', X_2 and X_2' = H, OH or $C_{1\sim5}$ substituted and unsubstituted alkyl groups)



Formula (20)

(where R_5 and R_6 = H, OH or $C_{1\sim5}$ substituted and unsubstituted alkyl groups; k' and m' = 1~5)



Formula (21)

(where R_1~R_5 = H, OH or $C_{1\sim10}$ straight or branched chain alkyl groups with possible substitutions, or $C_{1\sim10}$ straight or branched chain alkanol groups with possible substitutions)

Here, phenols are exemplified by, for example, phenol, cresol, xylenol, ethylphenol, propylphenol, butylphenol, resorcinol, pyrogallol, etc., and they may be used singly or in combination of two or more.

Also, dialkylbenzene glycols include p-xylene glycol dimethyl ether, p-xylene glycol, m-xylene glycol dimethyl ether, m-xylene glycol, o-xylene glycol dimethyl ether, o-xylene glycol, etc., and they may be used singly or in combination.

As a condensation catalyst, organic acids such as oxalic acid, p-toluenesulfonic acid, xylenesulfonic acid, phenolsulfonic acid, etc. and inorganic acids such as hydrochloric acid, sulfuric acid, etc. may be used. Amount of the catalyst to be added is in the range of 0.01~3.0 weight percent of the sum of phenols and dialkylbenzene glycols used for the reaction.

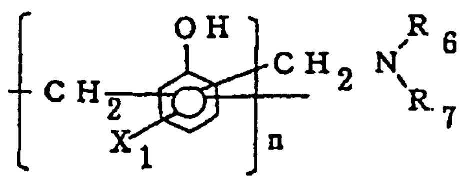
For each 1 mol of phenols having chemical formula (19) described above, the amount of dialkylbenzene glycols is preferably 0.02~0.6 mol, and more preferably 0.03~0.5 mol. When the amount of dialkylbenzene glycol exceeds 0.6 mol, the solution stability, for example, of the phenolic compound thus obtained in the metal surface treatment solution is reduced. Furthermore, the phenolic compound becomes insoluble in acid, often leading to the difficulty in performing the objective metal surface treatment. On the other hand, when the amount is less than 0.02 mol, the solubility of phenolic compounds obtained becomes high, leading to the reduction of amount of resin adhering to the treated surface, and resulting in the inferior corrosion resistance and sliding ability.

Also, for each 1 mol of phenols represented by chemical formula (19) described above, the most preferable sum of dialkylbenzene glycol and formaldehyde is 0.7~0.9 mol. When the sum of dialkylbenzene glycol and formaldehyde exceeds 0.9 mol, they are gelatinized during the polycondensation reaction. On the other hand, when the sum of dialkylbenzene glycol and formaldehyde is less than 0.7 mol, the solution viscosity (or molecular weight) of polycondensation product itself remains low to be too stable in solution, resulting in the reduced amount of resin adhering to the treated surface, and the inferior corrosion resistance and sliding ability of the treated surface.

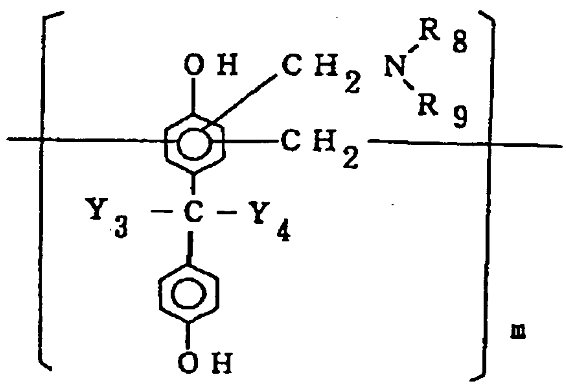
In addition, for each 1 mol of phenols represented by chemical formula (19) described above, the amount of amines having chemical formula (21) is preferably 0.5~2.0 mol, and more preferably 0.7~1.5 mol. When the amount of amines exceeds 2.0 mol, the solution stability becomes too good, resulting in the reduced amount of resin adhering to the treated surface and the inferior corrosion resistance and sliding ability of the treated surface. Furthermore, there is a possibility that unreacted amines and formaldehyde will remain, which may increase the load of sewage treatment. On the other hand, when the amount of amines is less than 0.5 mol, the hydrophobicity of phenolic compounds thus obtained becomes high, often resulting in reduced solution stability. And, in some cases, the phenolic compound may become insoluble in the metal surface treatment solution to make it impossible to perform surface treatment.

Here, amines include diethanolamine, N-methylaminoethanol, ketimine, diketimine, etc., and they may be used singly, or in combination of more than two kinds of them.

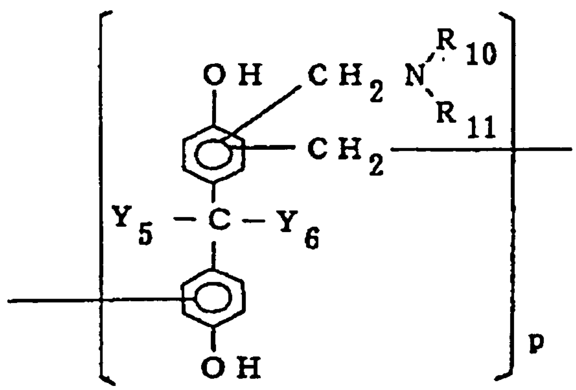
Also, other phenolic resins in accordance with the present invention is exemplified by a mixture of (e) a phenolic repeating unit containing at least more than one nitrogen atom represented by the following chemical formula (22) and (f) a bisphenolic repeating unit containing at least more than one nitrogen atom represented by the following chemical formulae (23) and (24). Weight ratio of resin composed of the phenolic repeating units (e) and that of the bisphenolic repeating units (f) described above is 90:10~10:90.



Formula (22)



Formula (23)



Formula (24)

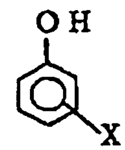
(where R_6, R_7, R_8, R_9, R_{10}, R_{11}, X_1, Y_3, Y_4, Y_5 and Y_6 = H, OH or $C_{1\sim10}$ straight or branched chain alkyl groups or $C_{1\sim10}$ straight or branched alkanol groups; m, n and p are 2~50, respectively. These alkyl and alkanol groups may be substituted with a functional group.)

The weight ratio of resins (e) and (f) in said mixture in accordance with the present invention is 90:10~10:90, and preferably 30:70~70:30. When the weight ratio of resin (e) exceeds said range, the external appearance turns brown or yellow after draining and drying. On the other hand, when the ratio of resin (f) exceeds the above range, corrosion resistance becomes inferior, though browning or yellowing are prevented.

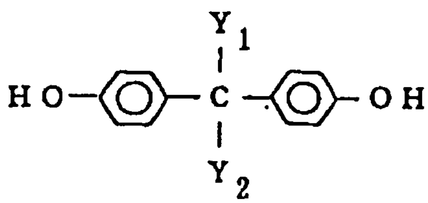
Also, the concentration of resins (e) and (f) described above in the metal surface treatment agent is 0.01~10 g/l, and more preferably 0.1~5 g/l. When the concentration of said mixture in the metal surface treatment agent is less than 0.01 g/l, the resinous coating film on the metal surface is not formed sufficiently thick, resulting in the reduced barrier effect and the inferior corrosion resistance and sliding ability. On the other hand, when the concentration exceeds 10

g/l, the resinous coating film becomes unnecessarily thick, resulting in the poor external appearance of the surface, as well as becoming expensive and less economical.

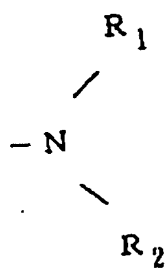
Furthermore, the phenolic resin of the present invention contains a copolymer composed of a phenolic compound (g) represented by the following chemical formula (25), a bisphenolic compound (h) represented by the following formula (26) and formaldehyde, and a phenol-bisphenol-formaldehyde copolymer or its salt linked with at least one kind of functional group represented by the following chemical formulae (27) and (28), wherein the molar ratio of the phenolic compound (g) and bisphenolic compound (h) described above is 9:1~1:9.



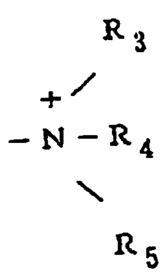
Formula (25)



Formula (26)



Formula (27)



Formula (28)

(where R_1, R_2, R_3, R_4, R_5, X, Y_1 and Y_2 = H, OH or $C_{1\sim10}$ straight or branched chain alkyl groups, or $C_{1\sim10}$ straight or branched chain alkanol groups. These alkyl or alkanol groups may be substituted with a functional group.)

The molar ratio of compounds (g) and (h) described above is 9:1~1:9, and preferably 3:7~7:3. When the molar ratio of compound (g) exceeds the above range, the external appearance turns brown or yellow after draining and drying. On the other hand, when the molar ratio of compound (h) becomes greater than the above range, corrosion resistance becomes inferior, though browning or yellowing are still prevented.

Also, the concentration of the above described copolymer in the metal surface treatment agent is 0.01~10 g/l, and preferably 0.1~5 g.

When the concentration of said copolymer in the metal surface treatment agent is less than 0.01 g/l, the thickness of resin coating film on the metal surface becomes insufficient and barrier effects are reduced, resulting in the inferior corrosion resistance and sliding ability. On the other hand, when the concentration exceeds 10 g/l, the resin coating film on the metal surface becomes unnecessarily thick, not only resulting in poor external appearance but also increasing costs and lowering economy.

As described above, by using the surface treatment agent containing phenolic resin, the sliding ability is superior, but the external appearance turns brown or yellow after draining and drying. On the other hand, the surface treatment agent containing bisphenolic resin has a problem that the corrosion resistance is inferior using this agent, although browning or yellowing after draining and drying are prevented.

The metal surface treatment agent of the present invention contains both phenolic and bisphenolic resins in a predetermined ratio, and is capable of forming a resinous coating film consisting of both resins which mutually compensate respective defects on the metal surface. Therefore, this agent is able to prevent surface browning or yellowing after draining and drying, and to improve sliding ability. Accordingly, the improved sliding ability leads to the prevention of jamming occurrence, and furthermore provides the sliding ability in the coil-coating. Also, since this agent can prevent turning the external appearance of coating film to brown or yellow, there is no possibility to cause any troubles in the succeeding process such as coating.

The metal surface treatment agent in accordance with the present invention may contain heavy metals. One or more of the following heavy metals may be contained: zirconium (Zr), titanium (Ti), molybdenum (Mo), tungsten (W), niobium (Nb), nickel (Ni), cobalt (Co), manganese (Mn), or tantalum (Ta), but preferable metals are zirconium (Zr), titanium (Ti), niobium (Nb), manganese (Mn), or tantalum (Ta). A supply source of these heavy metals is preferably their fluoride complex, or can also be their nitrate, phosphate, or the like.

The concentration of fluoride complex of heavy metal in the metal surface treatment agent in accordance with the present invention is preferably 0.01~10 g/l. When the concentration is less than 0.01 g/l, the corrosion resistance becomes inferior. On the other hand, when the concentration of fluoride complex of heavy metals exceeds 10 g/l, the corrosion resistance also becomes inferior.

Other metal surface treatment agents in accordance with the present invention contain an organic high molecular compound or its salt having more than one nitrogen atom or cationic sulfur atom and in a water-soluble, water-dispersive or emulsive form and also an oxidizing agent.

Organic high molecular compound

The content of said organic high molecular compounds in the metal surface treatment agent is preferably 0.01~10 g/l, and more preferably 0.1~5 g/l. When the content of said organic high molecular compound is less than 0.01 g/l, a sufficiently thick organic resinous coating film is not formed, resulting in the decrease in corrosion resistance due to the reduced barrier effect. On the other hand, when the organic high molecular compound content exceeds 10 g/l, the stability of the surface treatment solution is reduced because of the presence of said organic high molecular compound in excess in the treatment solution. Accordingly, the solution is expensive and uneconomical.

Oxidizing agent

As the oxidizing agent is effective in promoting the chemical stabilization of metal surface and the refinement and homogeneity of resinous coating film, it improves corrosion resistance. The oxidizing agent is selected from a group including hydrogen peroxide, nitrous acid, nitrite, perboric acid, perborate, chloric acid, chlorate, bromic acid, and bromate, and is preferably hydrogen peroxide and nitrite. The content of oxidizing agent in the metal surface treatment agent is preferably 0.01~10 g/l, and more preferably 0.1~2 g/l. When the content of the oxidizing agent is less than 0.01 g/l, the effect as oxidising agent is not exerted, and the corrosion resistance is inferior. On the other hand, when the content of oxidizing agent exceeds 10 g/l, effect as oxidising agent is reduced and it becomes uneconomical.

Also, the metal surface treatment agent of the present invention described above may further contain inorganic acid or heavy metal.

Inorganic acid

Inorganic acid may include phosphoric acid, nitric acid, or the like, with phosphoric acid being most preferable. Salt of these acids is preferably that of sodium, potassium, magnesium, etc. The concentration of phosphoric acid in the metal surface treatment agent is preferably 0.01~10 g/l, and more preferably 0.25~5 g/l. When the concentration is less than 0.01 g/l, acidity becomes insufficient and the organic high molecular compound described above becomes less soluble. On the other hand, when the concentration exceeds 10 g/l, resin precipitability is suppressed at the time of surface treatment and corrosion resistance becomes inferior.

Heavy metal

One or more of Nb, Ni, Co, Mn, Ti, Ta, Mo, or W, one or more than two kinds of them may be selected and combined. Fluoride complex of heavy metals described above is preferred, and nitrate and phosphate are also included. The content of heavy metal in the metal surface treatment agent is preferably less than 10 g/l. When the content of heavy metal exceeds 10 g/l, corrosion resistance, coating adhesiveness, and sliding ability are reduced.

Furthermore, the metal surface treatment agent in accordance with the present invention may contain water-soluble, water-dispersive, or emulsive organic high molecular compound described above, as well as phosphate ion and aluminum ion.

The content of organic high molecular compound as described above in the metal surface treatment agent is preferably 0.01~10 g/l, and more preferably 0.1~5 g/l. When the content of said organic high molecular compound is less than 0.01 g/l, the organic resinous coating film is not sufficiently thick, resulting in reduced barrier effect and decreased corrosion resistance. On the other hand, when the content of said organic high molecular compound exceeds 10 g/l, the organic resinous coating film becomes unnecessarily too thick, generating interference color on the treated material after the treatment, resulting in poor external appearance. Also the presence of said organic high molecular compound in excess in the treating bath reduces the stability of the surface treating bath, and the treatment becomes expensive and uneconomical.

Phosphate ions

A supply source of phosphate ions may be phosphoric acid or phosphate. The phosphate is preferably that of sodium, potassium, magnesium, or the like. Phosphate ions are used to acidify the aqueous solution, solubilize organic high molecular compounds described above, or etch the metal surface. The concentration of phosphate ions in the metal surface treatment agent is preferably 0.01~0.8 g /l. When the concentration of phosphoric acid is less than 0.01 g/l, etching is not only insufficient, but acidity also becomes insufficient, and the organic high molecular compounds described above become less soluble. Accordingly, the organic coating film is insufficiently precipitated on the metal surface, leading to inferior in corrosion resistance. On the other hand, when the concentration exceeds 0.8 g/l, the etching effect is not only saturated to an uneconomical extent, but also the phosphate ions increase the load for sewage treatment.

Aluminum ions

Aluminum ions are effective in accelerating the precipitation rate of resinous coating film (that is, coating film containing organic high molecular compounds), and promoting the refining and homogeneity of the coating film. A supply source of aluminum ions is aluminum nitrate, aluminum hydroxide and aluminum fluoride, and when the metal for surface treatment is aluminum alloy, aluminum ions eluted by etching process may be usable. The concentration of aluminum ions in the metal surface treatment agent is preferably 0.01 g/1~0.5 g/l, and more preferably 0.05 g/1~0.2 g/l. When the concentration of aluminum ions is less than 0.01 g/l, the organic high molecular compound described above is less readily precipitated to the metal surface, which resultingly has inferior corrosion resistance. On the other hand, when the concentration of aluminum ions exceeds 0.5 g/l, aluminum ions form insoluble materials with the organic high molecular compounds described above in the treatment solution, which becomes cloudy or produces sludge, resulting in inferior external appearance of the metal.

Also, the metal surface treatment agent in accordance with the present invention may contain water-soluble, water-dispersive or emulsive organic high molecular compounds together with polyvalent anions.

The concentration of the organic high molecular compound described above in the metal surface treatment agent is preferably 0.01~10 g/l, and more preferably 0.1~5 g/l. When the concentration of said organic high molecular compound is less than 0.01 g/l, a sufficiently thick organic resinous coating film is not formed, leading to inferior barrier effect and resulting in inferior corrosion resistance of the coating film. On the other hand, when the concentration of said organic high molecular compound exceeds 10 g/l, the organic resinous coating film is not only formed unnecessarily thick, but also generates interference color in the treated material after the surface treatment, resulting in inferior external appearance. Also, the unavoidable presence of said organic high molecular compound in excess in the treating bath not only reduces the stability of the surface treating bath, but also makes the process expensive and uneconomical.

Polyvalent anions

Polyvalent anions are exemplified by condensed phosphoric acid (pyrophosphoric acid, metaphosphoric acid, hexametaphosphoric acid, tripolyphosphoric acid, tetraphosphoric acid, etc.), molybdic acid, tungstic acid, vanadic acid, phosphomolybdic acid, phosphotungstic acid, silicotungstic acid, or the like, and their salts. The concentration of poly-

valent anions in the metal surface treatment agent is preferably 0.003 g/1~10.0 g/l, and more preferably 0.01 g/1~2 g/l. When the concentration of polyvalent anions is less than 0.003 g/l, etching of the metal surface becomes insufficient, and the resinous coating film is less readily precipitated to the metal surface, resulting in inferior corrosion resistance and sliding ability. On the other hand, when the concentration of polyvalent anions exceeds 10 g/l, not only the stability of the treatment solution, but also the corrosion resistance and sliding ability are reduced. Here, by the treatment solution is meant the metal surface treatment agent in accordance with the present invention or that appropriately diluted with water.

Also, the metal surface treatment agent in accordance with the present invention may contain the following etchant and etchant supplement, if necessary.

Etchant

Etchant is exemplified by hydrofluoric acid and its salt. The concentration of the etchant in the metal surface treatment agent is preferably 0.005 g/1~5 g/l. When the concentration of fluoride ions is less than 0.005 g/l, not only etching of the metal surface is reduced, but also pH elevation on the surface becomes insufficient. Accordingly, the resinous coating film is less readily precipitated to the metal surface and corrosion resistance is reduced. On the other hand, when the concentration of fluoride ions exceeds 5 g/l, etching on the metal surface is overly accelerated, and, in a similar manner as above, the resinous coating film is less readily precipitated to the metal surface, resulting in reduced corrosion resistance, as well as insufficient sliding ability.

Etchant supplement

As the etchant supplement, silicofluoric acid, borofluoric acid and their salts may be used. The concentration of the etchant supplement in the metal surface treatment agent is preferably 0.003 g/l~5 g/l. When the concentration of the etchant supplement is less than 0.003 g/l, etching of the metal surface is insufficient, and the resinous coating film becomes less readily precipitated to the metal surface, resulting in inferior corrosion resistance. On the other hand, when the concentration of the etchant supplement exceeds 5 g/l, etching is accelerated too much, and, in a similar manner as above, the resinous coating film is less readily precipitated the metal surface, resulting in reduced corrosion resistance, as well as insufficient sliding ability.

The metal surface treatment method of the present invention is the method wherein the metal surface is contacted with the metal surface treatment agent, then washed with water and dried.

Conditions and method for the treatment

The pH value of the metal surface treatment agent described above is about 2.0~5.0, and preferably 2.5~4.0. The pH is adjusted with NaOH, ammonia water, nitric acid, etc. Temperature for contacting the metal surface treatment agent of the present invention with metallic materials is preferably room temperature (for example, 20°C)~90°C, and more preferably 35~65°C. In general, the time for contacting metallic materials with the metal surface treatment agent in accordance with the present invention becomes shorter as the contacting temperature is raised.

The duration of spray coating of the metallic material is about 5 seconds ~5 min, and more preferably 10~60 seconds. When the immersion coating method is used, it requires a longer contacting time than the above. In addition, the metal surface may be contacted with the treatment agent by the dipping method, flow-coating method, rolling coating method, or the like.

As described above, metallic materials subjected to the conversion coating are washed with water, and dried at 150~240 °C. When the drying temperature is below 150°C, corrosion resistance is inferior.

In the following, the precipitation mechanism of the organic high molecular compound of the present invention to the metal surface will be described. When the organic high molecular compound described above contains atomic nitrogen (derived from amine), it becomes cationic in acidic solution. By the elevation of pH on the metal surface at the time of etching, this cationic nature of the compound is nullified, resulting in the aggregation and precipitation of the organic high molecular compound on the metal surface. Furthermore, the precipitation of resin to the metal surface is also caused by chelating the lone pair electrons of this nitrogen atom with metal.

Also, metallic materials used in the metal surface treatment method of the present invention are exemplified by, in addition to aluminum and aluminum alloy used for aluminum cans, iron, zinc, zinc alloy, tin-plated steel, stainless steel, etc.

As described above, using the metal surface treatment agent in accordance with the present invention, the nitrogen atom or cationic sulfur atom in the organic high molecular compound or its salt is coordinated to the metal surface, resulting in the improvement of coating adhesiveness and corrosion resistance. Furthermore, since the organic high molecular compound or its salt is almost homogeneously distributed on the metal surface, the friction resistance can be

reduced, and the sliding ability can be improved.

Therefore, by using the metal surface treatment agent in accordance with the present invention, the corrosion resistance and coating adhesiveness can be significantly improved as compared with the conventional agent, and a superior sliding ability can be provided.

Also, with the metal surface treatment composition in accordance with the present invention, jamming can be prevented in the fabrication of food cans using aluminum or its alloy, and sliding ability can be provided in the coil coating.

In addition, when the high molecular compound used in the present invention is a phenolic resin composition having the structure represented by the chemical formula (18) described above, this phenolic resin composition suppresses the hydrophilicity, resulting in the superior sliding ability of coating film. Furthermore, since the coating film contains few resinous skeletons, there is no possibility for the coating film to be colored, even though conjugated emission by phenol occurs in drying. Therefore, superior sliding ability can prevent the occurrence of jamming, and furthermore, provide sliding ability in the coil coating. Also, since the phenolic resin can prevent the discoloration of colored surface, no difficulty is expected in later processes, such as coating.

Also, according to the metal surface treatment agent and method of the present invention, by adjusting the ratio between the phenolic and bisphenolic components in the copolymer [consisting of (g) and (h)] or a mixture [consisting of (e) and (f)] described above within a specific range, browning of the external appearance of the treated object can be prevented, and, furthermore, the sliding ability, coating adhesiveness, and corrosion resistance of the surface can be improved.

In addition, according to the metal surface treatment agent and method in accordance with the present invention, by adding the oxidizing agent to the metal surface treatment agent containing the organic high molecular compound, the metal surface can be retained in a highly oxidized condition during the treatment, immobilized, and, accordingly, stabilized. Furthermore, the oxidizing agent accelerates etching rate of the metal surface in the treatment, leading to the acceleration of the pH elevation rate on the metal surface. Thus, the precipitation rate of the organic coating film is accelerated, leading to the formation of the fine organic (conversion) coating film on the metal surface. Therefore, the barrier ability (ionic permeability resistance, water permeability resistance) of the coating film is improved, resulting in the improved corrosion resistance prior to coating. Furthermore, since the coating film is mainly composed of the organic film, it has the sliding ability, and, although it contains some inorganic (metal salt) coating film which may cause the aggregate destruction, the organic coating film acts as the binder between the upper coating film and metallic material, resulting in the improved coating adhesiveness.

Also, according to the metal surface treatment agent and method in accordance with the present invention, as the organic high molecular compound contained in the metal surface treatment agent forms insoluble compound with aluminum ions, the precipitation rate of the organic coating film to the metal surface can be accelerated when aluminum ions are previously included in the metal surface treatment agent. Therefore, the organic coating film can be precipitated to the metal surface in the presence of lower concentration of phosphate ions than that in the conventional method. Furthermore, as a fine and homogeneous organic coating film can be formed on the metal surface by the presence of aluminum ions, the corrosion resistance, coating adhesiveness and sliding ability can be satisfied at the same time. In addition, since the concentration of phosphate ions can be reduced, an environment-friendly metal surface treatment agent can be provided.

In addition, according to the metal surface treatment agent and method in accordance with the present invention, the pH value for the resin precipitation can be shifted to the acidic side by supplementing the metal surface treatment agent containing organic high molecular compound with polyvalent anions. The organic high molecular compound described above is soluble in the acidic side of pH value, but aggregates and precipitates out from the aqueous solution system when the pH value shifts to the neutral range from the weak acidity. Therefore, the addition of polyvalent anions can accelerate the precipitation rate of organic coating film and increase the amount of resinous coating film derived from the organic high molecular compound described above to precipitate on the metal surface, leading to the shortening of the treating time. In addition, even with the relatively low amount of the coating film, since the fine coating film is formed on the metal surface, its corrosion resistance prior to coating (blackening resistance in boiling water in the case of aluminum DI cans) is improved. Furthermore, since the coating film is mainly organic, coating adhesiveness is improved, even though some inorganic components (metal salts) are contained that have sliding ability which may lead to aggregate destruction.

Optimum embodiments for performing the invention

In the following, the present invention will be described with reference to actual and comparative examples.

Actual Examples 1~23 and Comparative Examples 1~12

1. Objects to be treated

Shaped cans fabricated from aluminum alloy plate in Al-Mn series (JIS-A3004) using DI techniques, etc.

2. Method for evaluating the undercoating film

a) Blackening resistance in boiling water

Objects treated with the composition in the present actual and comparative examples were submerged in boiling tap water for 30 min, and then the external appearance was evaluated according to the following scale.

Excellent: No change in external surface
Good : Surface slightly blackened
Poor : Surface blackened

b) Sliding ability of the undercoating film

Motion frictional coefficient of objects subjected to the conversion treatment by the method of the present actual examples was determined using a "Heidon-14" tester with the load of 50 g and touching needle speed of 300 mm/min.

Excellent: Frictional coefficient less than 0.6.
Average : Frictional coefficient 0.6~0.8.
Poor : Frictional coefficient greater than 0.8.

c) Coating adhesiveness

Objects to be treated were coated with a paint (BASF Co., EB-70-001N 150 mg/m^2/EB-69-002N 60 mg/m^2) using a bar coater. The coated objects were subjected to wedge-bending. An adhesive tape ("cellotape", Nichiban Co.) was stuck to the bent portion, and then peeled off. The peeling conditions were evaluated according to the following scale.

Excellent: Width of coating film peeled off by tape less than 15 mm.
Average: Width of coating film peeled off by tape 15~20 mm.
Poor : Width of coating film peeled off by tape greater than 20 mm.

3. Conditions for metal surface treatment

Actual Example 1:

Shaped cans of Al-Mn series (JIS-A3004) were spray-degreased using an acidic degreasing agent (Surfcleaner NHC250, Nippon Paint Co., Ltd., 30 g/l) at 75°C for 60 seconds and washed with water. The cans were then subjected to a spray treatment at 50°C for 20 seconds with a treatment solution shown in Table 2, which was prepared by dissolving the water-soluble organic high molecular compound A-1 shown in Table 1 (0.2 g/l) in an aqueous solution prepared by diluting a treatment agent of zirconium phosphate series (Alsurf 440, Nippon Paint Co., Ltd.) to a concentration of 20 g/l. After the spray treatment, the cans were washed with tap water, and then dried at 190°C for 2 min.
Results of the evaluation are shown in Table 3.

Actual Examples 2~12 and Comparative Examples 1~4:

In actual examples 2~12 and comparative examples 1~4 were used metal surface treatment compositions comprising water-soluble organic high molecular compounds (shown in Table 1) and fluoride complexes of heavy metal in the combination ratio shown in the following Table 3, and the metal surface treatment was performed with these compositions according to the actual example 1.

Table 1

Water-soluble organic high molecular compound			
	Copolymer	Mixing ratio (weight ratio)	Molecular weight (Mw)
A-1	HEA*1/p-TBS*2/DMAEA*3	40/30/30	3,000
A-2	HEMA*4/St*5/DMAPMA*6	60/20/20	2,500
A-3	HEA/MMA*7/St/DMAEA	50/10/20/20	4,000
A-4	HPA*8/St/AAm*9	50/30/20	2,000
A-5	HEA/VP*10/DMAEA	60/20/20	3,000
A-6	HEA/EHA*11/VP/DMAPMA	40/20/15/15	1,500
B-1	HEA/p-TBS	70/30	4,000

*1: HEA hydroxyethyl acrylate
*2: p-TBS para-t-butylstyrene
*3: DMAEA N-dimethylaminoethyl acrylate
*4: HEMA hydroxyethyl methacrylate
*5: St styrene
*6: DMAPMA N-dimethylaminopropyl methacrylamide
*7: MMA methyl methacrylate
*8: HPA hydroxypropyl acrylate
*9: AAm acrylamide
*10: VP vinyl phenol
*11: EHA 2-ethylhexyl acrylate

Table 2

		Water-soluble organic high molecular compound		Heavy metal compound	
		Compound	Content (g/l)	Compound	Concentration (g/l)
Actual example	1	A-1	0.2	Alsurf 440*1	20
	2	A-2	0.5	Alsurf 440	20
	3	A-3	1	Alsurf 440	20
	4	A-4	0.5	Alsurf 440	20
	5	A-5	0.2	Alsurf 440	20
	6	A-6	0.2	Alsurf 440	20
	7	A-1	0.2	$[NH_4]_2ZrF_6$	1
	8	A-1	0.2	$[NH_4]_2TaF_6$	1
	9	A-1	0.2	$[NH_4]_2NbF_6$	1
	10	A-1	0.2	$[NH_4]_2MnF_6$	1
	11	A-1	0.01	Alsurf 440	20
	12	A-1	10	Alsurf 440	20
Comparative example	1	B-1	0.2	Alsurf 440	20
	2	A-1	0.2	$[NH_4]_2TiF_6$	1
	3	A-1	0.2	$[NH_4]_2ZnF_6$	1
	4	-	-	Alsurf 440	20

*1: Alsurf 440: Treatment agent of zirconium phosphate series (Nippon Paint Co.)

Table 3

		Result of Evaluation			
		Blackening resistance in boiling water	Sliding ability (motion frictional coefficient)		Coating adhesiveness
Actual example	1	Excellent	Excellent	0.49	Excellent
	2	Excellent	Excellent	0.48	Excellent
	3	Excellent	Excellent	0.47	Excellent
	4	Excellent	Excellent	0.48	Excellent
	5	Excellent	Excellent	0.45	Excellent
	6	Excellent	Excellent	0.46	Excellent
	7	Excellent	Excellent	0.48	Excellent
	8	Excellent	Excellent	0.49	Excellent
	9	Excellent	Excellent	0.48	Excellent
	10	Excellent	Excellent	0.48	Excellent
	11	Excellent	Excellent	0.49	Excellent
	12	Excellent	Excellent	0.49	Excellent
Comparative example	1	Poor	Poor	0.90<	Poor
	2	Poor	Excellent	0.51	Excellent
	3	Poor	Excellent	0.52	Excellent
	4	Excellent	Poor	0.90<	Poor

These results indicated that, by using the metal surface treatment composition of the present invention, all the examined characteristics, including blackening resistance in boiling water, sliding ability, and coating adhesiveness were improved as compared with the conventional composition.

Actual Example 13:

Shaped cans of Al-Mn series (JIS-A3004) were degreased using an acidic degreasing agent (Surfcleaner NHC250, Nippon Paint Co., Ltd.); 30 g/l, 75°C, 60 seconds with a sprayer) and washed with water. Then, the cans were subjected to a spray conversion treatment at 50°C for 20 seconds with a treatment solution shown in Table 5 prepared by dissolving a water-soluble resin C-1 shown in Table 4 (0.2 g/l) in an aqueous solution which had been prepared by diluting a treatment agent of zirconium phosphate series (Alsurf 440, Nippon Paint Co., Ltd.) to a concentration of 20 g/l. After the spray treatment, the cans were washed with tap water, and then dried at 190°C for 2 min. Results of the evaluation are shown in Table 6.

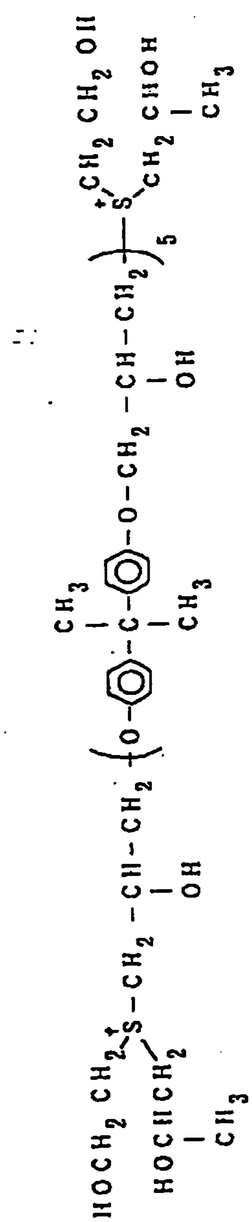
Actual Examples 14~23 and Comparative Examples 5~12:

In actual examples 14~23 and comparative examples 5~12, the metal surface treatment compositions containing water-soluble resins (shown in Table 4) and fluorides of heavy metals in composition ratios shown in the following Table 5 were used for the treatment according to Actual Example 13 described above. Results of the evaluation are shown in Table 6.

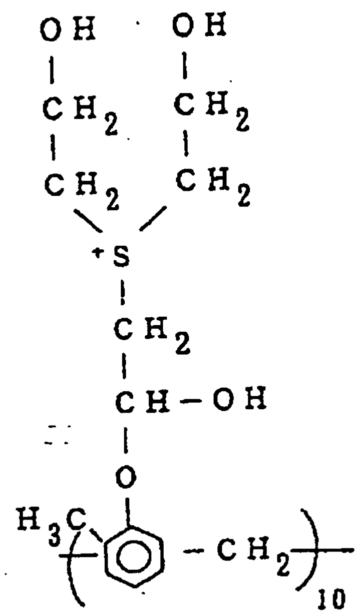
Table 4

Water-soluble organic high molecular compound		
	Structure	Molecular weight (Mr)
C-1	Bisphenol A type epoxy resin supplemented with sulfonyl group	1,800
C-2	Novorac type epoxy resin modified with sulfonium group	2,500
C-3	Vinyl phenolic resin modified with sulfonium group	4,600
C-4	Bisphenol A type epoxy resin modified with sulfonium group	2,000
D-1	Compound represented by the chemical formula (13)	20,000
D-2	Bisphenol A type epoxy resin ring-opened by alcohol	460
D-3	Bisphenol A type epoxy resin modified with sulfonium group	610

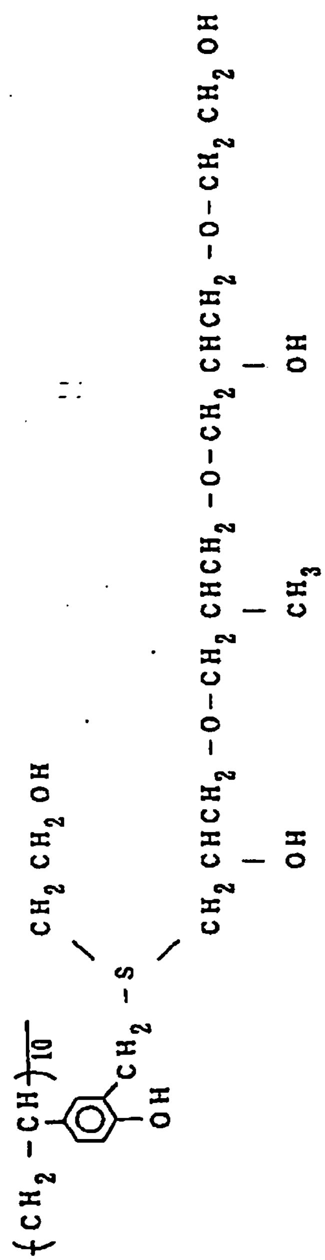
Formula C-1



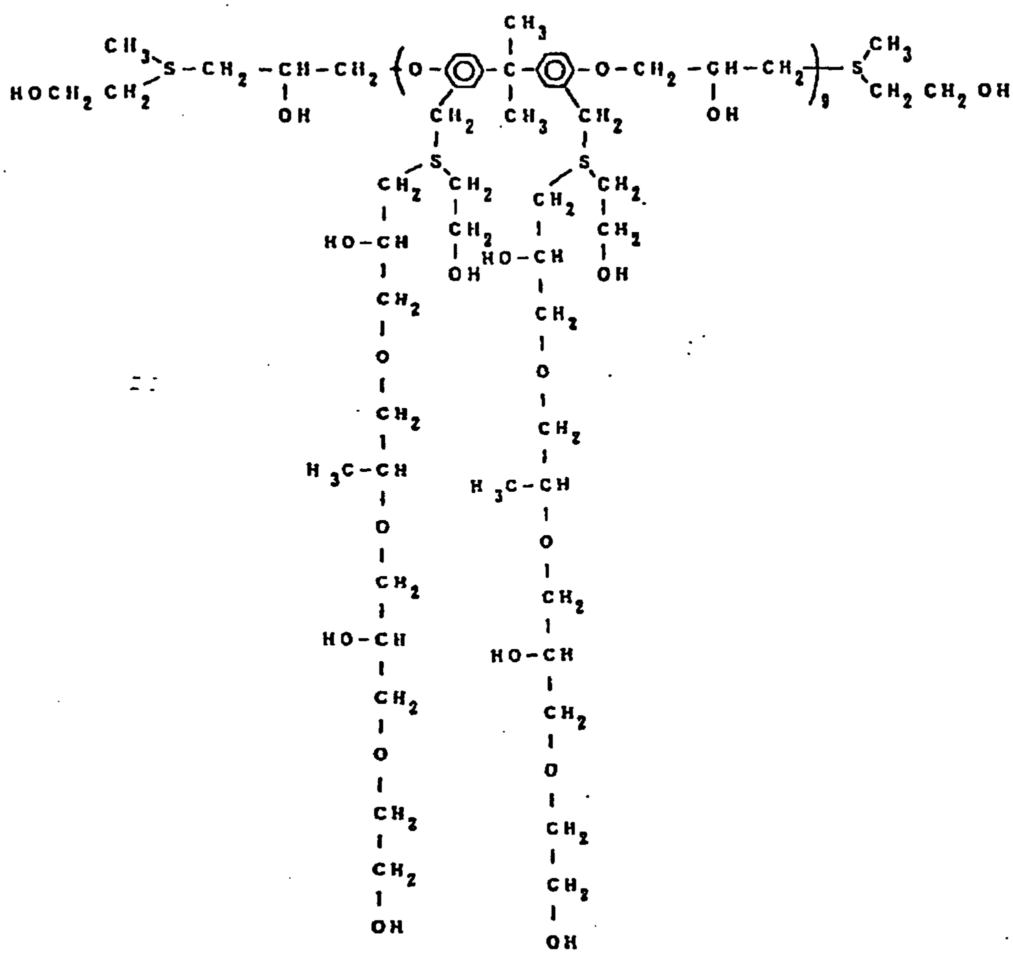
Formula C-2



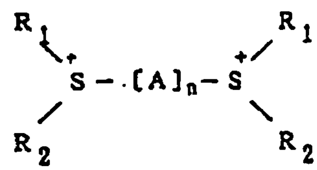
Formula C-3



Formula C-4

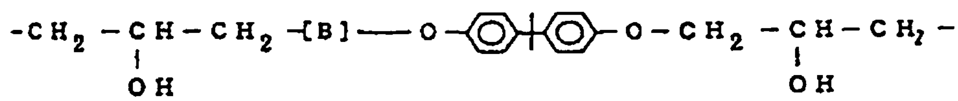


Formula D-1



(where

A =



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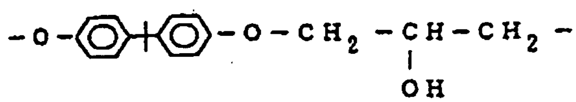
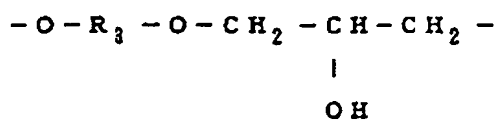


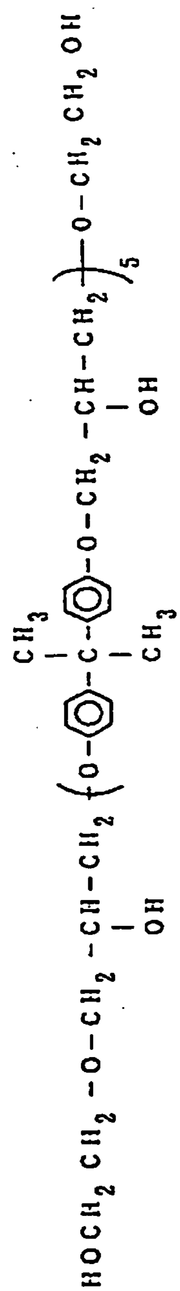
or



R_1 and R_2 = H, OH or $C_{1\sim15}$ straight or branched chain alkyl groups with possible substitutions, or $C_{1\text{-}15}$ straight or branched alkanol groups with possible substitutions

R_3 = $C_{10\sim18}$ straight or branched chain alkyl groups

Formula D-2



Formula D-3

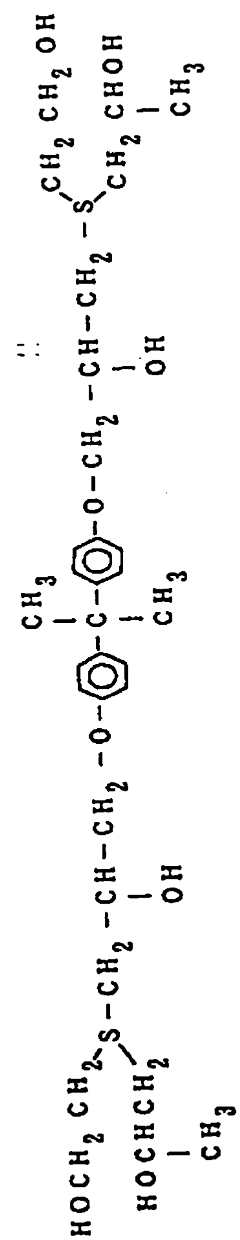


Table 5

		Cationic organic high molecular compound		Heavy metal compound	
		Compound	Content (g/)	Compound	Content
Actual example	13	C-1	0.2	Alsurf 440[*1]	20
	14	C-2	0.2	Alsurf 440	20
	15	C-3	0.2	Alsurf 440	20
	16	C-4	0.2	Alsurf 440	20
	17	C-1	0.2	$[NH_4]_2ZrF_6$	1
	18	C-1	0.2	$[NH_4]_2TaF_6$	1
	19	C-1	0.2	$[NH_4]_2NbF_6$	1
	20	C-1	0.2	$[NH_4]_2MnF_6$	1
	21	C-1	0.2	$[NH_4]_2CoF_6$	1
	22	C-1	0.01	Alsurf 440	20
	23	C-1	5	Alsurf 440	20
Comparative example	5	D-1	0.2	Alsurf 440	20
	6	D-2	0.2	Alsurf 440	20
	7	C-1	0.2	$[NH_4]_2TiF_6$	1
	8	C-1	0.2	$[NH_4]_2ZnF_6$	1
	9	-	-	Alsurf 440	20
	10	D-3	0.2	Alsurf 440	20
	11	C-1	0.005	Alsurf 440	20
	12	C-1	10	Alsurf 440	20

*1: Alsurf 440 Treatment agent of zirconium phosphate series (Nippon Paint Co., Ltd.)

Table 6

Evaluation results					
		Blackening resistance in boiling water	Sliding (motion frictionalability coefficient)		Coating adhesiveness
Actual example	13	Excellent	Excellent	0.45	Excellent
	14	Excellent	Excellent	0.42	Excellent
	15	Excellent	Excellent	0.49	Excellent
	16	Excellent	Excellent	0.41	Excellent
	17	Excellent	Excellent	0.45	Excellent
	18	Excellent	Excellent	0.46	Excellent
	19	Excellent	Excellent	0.46	Excellent
	20	Excellent	Excellent	0.44	Excellent
	21	Excellent	Excellent	0.45	Excellent
	22	Excellent	Excellent	0.49	Excellent
	23	Excellent	Excellent	0.43	Excellent
Comparative example	5	Average	Average	0.69	Poor
	6	Poor	Poor	0.90<	Poor
	7	Poor	Excellent	0.45	Excellent
	8	Poor	Excellent	0.45	Excellent
	9	Excellent	Poor	0.90<	Poor
	10	Poor	Average	0.74	Average
	11	Poor	Poor	0.79	Poor
	12	Average	Excellent	0.42	Excellent

These results indicate that, by using the metal surface treatment composition of the present invention, all the examined characteristics, including blackening resistance in boiling water, sliding ability, and coating adhesiveness were improved as compared with those by using the conventional composition.

In the following, preferred embodiments wherein the high molecular compounds are phenolic resins in accordance with Claims 6, 7, and 8 will be described.

Actual Examples 24~33 and Comparative Examples 13~18:

〈Preparation of polycondensation product E〉

The reaction was performed with the reactants in the mixing ratio shown in Table 7. Into a reaction apparatus equipped with a stirrer, reflux condenser, and thermometer were placed m-cresol (1 mol, 108 g), m-xylene glycol dimethyl ether (0.03 mol, 5 g). There were p-toluenesulfonic acid (0.3 g). These were reacted at 160°C for 2 h. The interior temperature was reduced to 100°C, and, to the reaction mixture was added a 37% formaldehyde aqueous solution (0.75 mol, 61 g) over 1 h. The resulting mixture was refluxed at 100°C for 2 h, and then subjected to dehydration reaction at up to 140°C under normal pressure and then in vacuo. The polycondensation reaction was judged to be completed when the inside temperature elevated up to 160°C. Then, as shown in Table 8, the reaction mixture was cooled to 120°C, and added with butyl cellosolve (194 g) to dissolve the polycondensation product completely. To the resultant mixture was added pure water (194 g) below 100°C, and, when the inside temperature was reduced to 50°C, N-methylaminoethanol (1 mol, 75 g) was added. To this mixture was added a 37% formaldehyde aqueous solution (1 mol, 81.1 g) over 1 h, and the resultant mixture was reacted at 50°C for 1 h, and further at 90°C for 1.5 h. The resin solution thus obtained had the viscosity 0.11 Pa • s, contained free formaldehyde 0%, free phenol 0%, left non-volatile residue 31.2%

after heating at 180°C for 1 h, and was soluble in phosphoric acid aqueous solution at pH 2.

(Preparation of Polycondensation Products F~H)

The reaction was performed, according to the method for preparing polycondensation product E, with reactants in the mixing ratio shown in Tables 7 and 8, and the resin solution having the general properties shown in Table 8 was obtained.

(Preparation of Polycondensation Product I)

The reaction was performed with reactants in the mixing ratio shown in Table 7. Into a reaction apparatus equipped with stirrer, reflux condenser, and thermometer were placed phenol (1 mol, 94 g) and p-toluenesulfonic acid (0.3 g), and, after the inside temperature was raised to 100°C, a 37% formaldehyde aqueous solution (0.8 mol, 65 g) was added to the mixture over 1 h, and the resultant mixture was refluxed at 100°C for 2 h. Then, the reaction mixture was subjected to the dehydration reaction at up to 140°C under the normal pressure, then in vacuo, and the polycondensation reaction was judged to be completed when the inside temperature-elevated to 160°C. Then, as shown in Table 8, the inside temperature was reduced to 120°C, and butyl cellosolve (156 g) was added to the mixture to dissolve the polycondensation product completely. Pure water (156 g) was added to the mixture below 100°C, and when the inside temperature was lowered to 50°C, N-methylaminoethanol (1 mol, 75 g) was added. To this mixture was added a 37% formaldehyde aqueous solution (1 mol, 81.1 g) over 1 h, and the resultant mixture was reacted at 50°C for 1 h, and further at 90°C for 3.5 h. The resin solution thus obtained had viscosity 0.12 Pa • s, contained free formaldehyde 0%, free phenol 0%, left non-volatile fraction 31.2% after heating at 180°C for 1 h, and was soluble in phosphoric acid ate aqueous solution at pH 2.

Preparation of Polycondensation Products J and K:

The reaction was performed according to the method for preparing the polycondensation product E with reactants in the mixing ratio shown in Tables 7 and 8, and a resin solution having the general properties shown in Table 8 was obtained.

Preparation of Polycondensation Product L:

The reaction was performed with reactants in the mixing ratio shown in Table 7. Into a reaction apparatus equipped with stirrer, reflux condenser, and thermometer were placed butyl cellosolve (200 g) and polyvinylphenol [molecular weight in weight average (Mr) = 3,000] (1 mol, 120 g, the repeating phenolic unit taken as 1 mole of the phenolic resin), and the mixture was stirred for 1 h as the inside temperature raised up to 110°C to dissolve the polyvinylphenol completely. When the inside temperature was reduced to 100°C, diethanolamine (1 mol, 105 g) was added, and the mixture was reacted at 50°C for 1 h, then at 90°C for 3 h. The resin solution thus obtained had a viscosity 0.12 Pa • s, free formaldehyde 0.7%, free phenol 0%, and left the non-volatile fraction 30.3% after heating at 180°C for 1 h, and was soluble in phosphoric acid aqueous solution at pH 2.

Table 7										
Polycondensation reaction			Polycondensation product				Polycondensation product			
			E	F	G	H	I	J	K	L
Mixing ratio Weight (mol)	Phenol	Phenol	-	94(1.0)	94(1.0)	-	94(1.0)	94(1.0)	94(1.0)	-
		m-Cresol	108(1.0)	-	-	-	-	-	-	-
		3,5-Xylenol	-	-	-	122(1.0)				
		Polyvinylphenol	-	-	-	-	-	-	-	120(1.0)
	Xylene glycol *1	PXDM	-	10(0.06)	40(0.24)	-	-	40(0.24)	40(0.24)	-
		OXDM	-	-	-	83(0.5)	-	-	-	-
		MXDM	5(0.03)	-	-	-	-	-	-	-
	Catalyst	p-Toluenesulfonic acid	0.3	0.3	0.3	-	0.3	0.3	-	-
		Phenolsulfonic acid	-	-	-	0.3	-	-	0.3	-
	37% formaline	*2	61(0.75)	57(0.7)	41(0.5)	16(0.2)	65(0.8)	41(0.5)	41(0.5)	-
Reaction time (h)	Primary reaction	160°C(h)	2	2	3	3		3	3	-
	Secondary reaction	100°C (h)	1	1	1	0.5	1.5	1	1	-

*1 PXDM: p-xylene glycol dimethyl ether

OXDM: o-xylene glycol dimethyl ether

MXDM: m-xylene glycol dimethyl ether

*2 Figures in parentheses represent the molar amount of formaldehyde.

Table 8

Aminomethylation reaction			Polycondensation product				Polycondensation product			
			E	F	G	H	I	J	K	L
Mixing ratio Weight (mol)	Solvent	Ethyl cellosolve	-	-	-	247	-	197	-	-
		Butyl cellosolve	194	173	197	-	172	-	360	200
		Pure water	183	149	170	230	161	193	335	189
	Amine	N-Methylaminoethanol	75(1.0)	60(0.8)	113(1.5)	-	75(1.0)	-	-	-
		Diethanolamine	-	-	-	158(1.5)	-	42(0.4)	231(2.2)	75(1.0)
	37% formalin	*1	81(1.0)	65(0.8)	122(1.5)	122(1.5)	81(1.0)	32(0.4)	178(2.2)	82(1.0)
Reaction time (h)	Tertiary reaction	50°C (h)	1	1	1	1	1	1	1	1
	Quaternary reaction	90°C (h)	1.5	1.5	2.	4	3.5	3	4.5	3
General property (unit)	External appearance		Reddish brown liquid	Reddish brown liquid	Reddish brown liquid	Reddish brown liquid	Reddish brown liquid	Reddish brown liquid	Reddish brown liquid	Reddish brown liquid
	Viscosity	(Pa · s)	0.11	0.13	0.09	0.15	0.12	0.09	0.18	0.12
	Free formaldehyde	(%)	0	0	0	0	0.6	0	1.1	0.7
	Free phenol	(%)	0	0	0	0	0.2	0.6	0	0
	Non-volatile fraction	(%)	31.2	30.0	33.0	34.6	31.2	28.2	30.1	30.3
	Acid solubility	*2	Excellent	Excellent	Excellent	Excellent	Excellent	Poor	Excellent	Excellent

*1: Figures in parentheses represent the molar amount of formaldehyde.

*2: Solubility of resin which is added to phosphoric acid aqueous solution at pH 2 such that the concentration of non-volatile fraction is adjusted to be 0.2 weight percent.

1. Objects to be treated

Cans fabricated by shaping an aluminum alloy plate of Al-Mn series (JIS-A3004) using DI techniques.

2. Method for evaluating the undercoating film

a) Blackening resistance in boiling water

Cans which had been treated with the agent of the present actual and comparative examples were immersed in boiling tap water for 30 min, and their external appearance was evaluated according to the following scale.

Excellent: No change in external appearance.
Average: External surface slightly blackened.
Poor: External surface blackened.

b) Sliding ability of the undercoating film

Motion frictional coefficient of the surface of cans treated by the method of the present actual example was determined using a Heidon-14 tester with a load of 50 g and a touching needle speed of 300 mm/min.

Excellent : Motion frictional coefficient less than 0.7.
Average : Motion frictional coefficient 0.7~0.8.
Poor : Motion frictional coefficient greater than 0.8.

c) Coating adhesiveness

Treated cans were painted with paint (BE-70-001N 150 mg/m^2/EB-69-002N 60 mg/m^2; BASF Co.) using a bar coater. Cans thus painted were subjected to wedge-bending, and an adhesive tape (Nichiban cellotape) was stuck onto the bent portion, and then peeled off. The peeling conditions were evaluated according to the following scale.

Excellent : Length of coating film peeled off with tape less than 15 mm.
Average : Length of coating film peeled off with tape 15~20 mm.
Poor : Length of coating film peeled off with tape greater than 20 mm.

d) Preserbility of treated external appearance (stainability)

The external appearance of cans, which had been subjected to conversion coating treatment and dried at 210°C for 3 min, was observed with the naked eye and evaluated.

Excellent : No stain
Poor : Stained

e) Stability of the treatment solution

The conditions of the freshly prepared treatment solution were observed with the naked eye.

Excellent : No white cloudiness
Average : White cloudy
Poor : Precipitates and aggregates are present.

f) Possibility of water pollution

Possibility of water pollution was evaluated with the total percent of free phenol and formaldehyde contained in the resinous solution.

Excellent : Total percent is less than 0.5%.
Average : Total percent is 0.5~5%.
Poor : Total percent exceeds 5%.

3. Conditions for treatment

shaped cans of Al-Mn series (JIS-A3004) were spray-degreaseed using an acidic degreasing agent (Surfcleaner

NHC250, Nippon Paint Co., Ltd.; 30 g/l) at 75°C for 60 seconds, washed with water. Then, the cans were subjected to spray conversion treatment at 50°C for 20 seconds with a surface treatment agent having a composition shown in Table 9 at pH 3.5, washed with water, and dried at 190°C for 2 min. Results of the evaluation are shown in Table 10.

Table 9

		Composition of metal surface treatment agent						
		Polycondensation product (g/l)	Phosphoric acid (g/l)	Hydrofluoric acid (g/l)	Hydrogen peroxide (g/l)	Tripolyphosphoric acid (g/l)	Silicofluoric acid (g/l)	Zircofluoric acid (g/l)
Actual example	24	E 1.0	0.5	0.5	-	-	-	-
	25	F 1.0	0.5	0.5	-	-	-	-
	26	G 1.0	0.5	0.5	-	-	-	-
	27	H 1.0	0.5	0.5	-	-	-	-
	28	E 1.0	0.5	0.5	0.1	-	-	-
	29	E 1.0	0.5	0.5	0.1	0.1	-	-
	30	E 1.0	0.5	0.5	-	-	0.01	-
	31	E 9	5	-	-	-	-	-
	32	E 0.05	0.1	0.1	-	-	-	-
	33	E 0.2	0.03	-	-	-	-	0.03
Comparative example	13	I 1.0	0.5	0.5	-	-	-	-
	14	J 1.0	0.5	0.5	-	-	-	-
	15	K 1.0	0.5	0.5	-	-	-	-
	16	L 1.0	0.5	0.5	-	-	-	-
	17	E 0.001	0.5	0.5	-	-	-	-
	18	E 1.0	20	-	-	-	-	-

Table 10

		Evaluation					
		Blackening resistance	Sliding ability	Coating adhesiveness	Maintenance of external appearance (stainability)	Stability of treatment solution	Water pollution
Actual example	24	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
	25	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
	26	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
	27	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
	28	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
	29	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
	30	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
	31	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
	32	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
	33	Excellent	Excellent	Excellent	Excellent	Excellent	Excellent
Comparative example	13	Average	Poor	Excellent	Poor	Excellent	Average
	14	-	-	-	-	Poor	Average
	15	Excellent	Excellent	Excellent	Excellent	Excellent	Average
	16	Average	Poor	Average	Average	Excellent	Average
	17	Poor	Poor	Poor	Excellent	Excellent	Excellent
	18	Poor	Excellent	Poor	Poor	Poor	Poor

These results indicate that, using the agent and method of the metal surface treatment of the present invention, all the characteristics, including corrosion resistance (blackening resistance in boiling water, and retorting resistance), sliding ability, and coating adhesiveness, of the metallic materials were much improved as compared with those treated with the conventional agents and methods.

In the following, preferred embodiments wherein high molecular compounds used in the present invention are phenolic resins according to Claims 9 and 10 will be described.

Actual Examples 34~41 and Comparative Examples 19~22:

1. Objects to be treated

Cans fabricated by shaping an aluminum alloy plate of Al-Mn series (JIS-A3004) using DI techniques, etc.

2. Method for evaluating the undercoating film

a) Blackening resistance in boiling water (corrosion resistance)

Cans which had been surface-treated with the composition of the present actual and comparative examples were

immersed in boiling water for 30 min, and their external appearance was evaluated according to the following scale.

Excellent : No change in external appearance
Average : External surface slightly blackened.
Poor : External surface blackened.

b) Sliding ability of the undercoating film surface

The motion frictional coefficient of cans surface-treated by the method of the present actual example was determined using a Heidon-14 tester with 5 mmØ steel ball, a load of 50 g and a touching needle speed of 300 mm/min.

Excellent : Motion frictional coefficient less than 0.5.
Average : Motion frictional coefficient 0.55~0.8.
Poor : Motion frictional coefficient greater than 0.8.

c) Coating adhesiveness

Surface-treated cans were painted with paint [EB-70-001N 150 mg/m^2; Clear, EB-69-002N 60 mg/m^2 (BASF Co.)] using a bar coater. Cans thus painted were subjected to wedge-bending, and an adhesive tape (Nichiban cellotape) was stuck onto the bent portion, then peeled off. Peeling conditions were evaluated according to the following scale.

Excellent : Length of coating film peeled off with tape less than 15 mm.
Average : Length of coating film peeled off with tape 15~20 mm.
Poor : Length of coating film peeled off with tape greater than 20 mm.

d) Browning resistance (stainability)

The external appearance of treated cans which had been drained and dried was observed with the naked eye.

Excellent : No browning
Average : Slightly browned
Poor : Browned

3. Conditions for metal surface treatment

Actual Example 34:

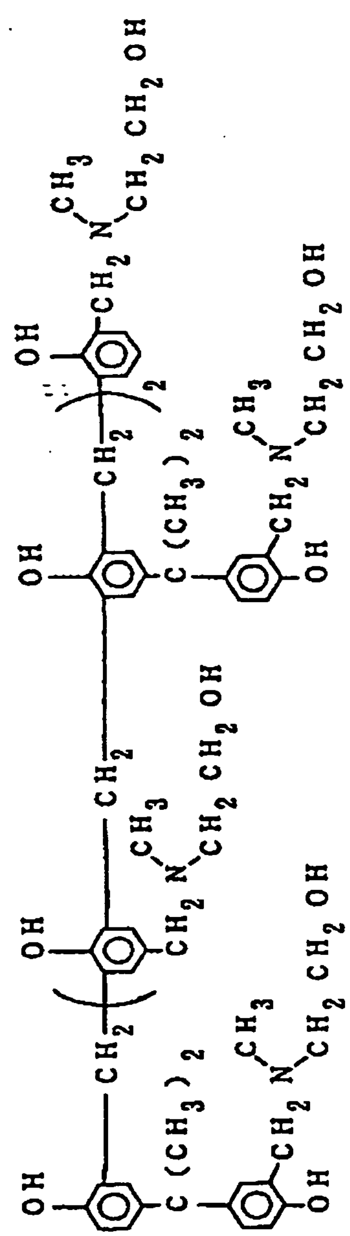
Shaped cans of Al-Mn series (JIS-A3004) were spray-degreased using an acidic degreasing agent (Surfcleaner NHC250, Nippon Paint Co.,Ltd.) at the concentration of 30 g/l at 75°C for 60 s, and washed with water. Then, the cans were subjected to a spray conversion treatment at 50°C for 20 s with a metal surface treatment agent containing phosphoric acid (0.5 g/l), hydrofluoric acid (0.5 g/l), pyrophosphoric acid (0.5 g/l) and the copolymer [phenol:bisphenol = 3:3 (mol/mol)] (0.6 g/l) and adjusted to pH 3.5. Treated cans were washed with water, drained and dried at 190°C for 2 min. Results of the evaluation are shown in Table 11.

Table 11									
		Composition of copolymer in the metal surface treatment agent			Evaluation item				
		Copolymer	Amount of copolymer added (g/l)	Phenol/bisphenol (mol/mol)	Blackening resistance in boiling water	Sliding ability	Coating adhesiveness	Browning resistance
Actual example	34	(29)	0.6	3:3	Excellent	Excellent	Excellent	Excellent
	35	(30)	1.5	2:6	Excellent	Excellent	Excellent	Excellent
	36	(31)	5.0	7:2	Excellent	Excellent	Excellent	Excellent
	37	(32)	9.5	4:5	Excellent	Excellent	Excellent	Excellent
Comparative example	19	(33)	5.0	1:0	Excellent	Excellent	Excellent	Poor
	20	(34)	5.0	0:1	Poor	Average	Excellent	Excellent

〈Synthesis of copolymer having the chemical formula (29)〉

In the following, the method for synthesizing a copolymer having the chemical formula (29) will be described.

Formula (29)



Molar ratio of phenol/bisphenol = 3:3

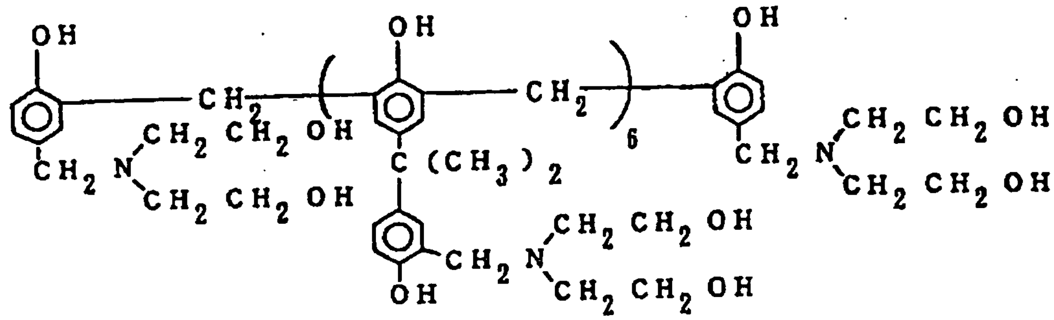
Into a reaction apparatus equipped with stirrer, reflux condenser, and thermometer were placed phenol (3 mol, 282 g), bisphenol A (3 mol, 684 g) and p-toluenesulfonic acid (0.3 g), and reacted at 160°C for 2 h. The inside temperature was then reduced to 100°C, and, to the reaction mixture was added a 37% formaldehyde aqueous solution (5 mol as

formaldehyde, 406 g) over 1 h. The resulting mixture was refluxed at 100°C for 2 h, and then subjected to the dehydration reaction at up to 140°C under the normal pressure, then in vacuo. The polycondensation reaction was judged to be completed when the inside temperature elevated to 160°C. The inside temperature was then reduced to 120°C, and butyl cellosolve (1,650 g) was added to dissolve the polycondensation product completely. To the resultant mixture was added pure water (1,650 g) at below 100°C, and, when the inside temperature was reduced to 50°C, N-methylaminoethanol (6 mol, 450 g) was added. To this mixture was added a 37% formaldehyde aqueous solution (6 mol, 486.6 g) over 1 h, and the resultant mixture was reacted at 50°C for 1 h, and further at 90°C for 1.5 h. The resin solution thus obtained had a viscosity 0.15 Pa • s, contained free formaldehyde 0%, free phenol 0%, left non-volatile fraction 31.1% after heating at 180°C for 1 h, and was soluble in phosphoric acid aqueous solution at pH 2.

Actual Examples 35~37 and Comparative Examples 19~20:

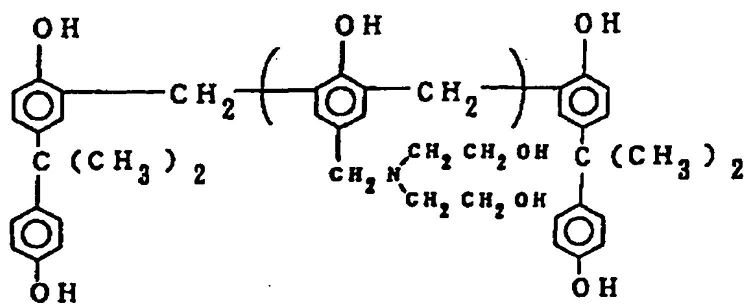
Surface treatment was performed using metal surface treatment agents wherein molar ratios of phenol/bisphenol in the copolymers having the following chemical formulae (30)~(34) as well as amounts of these copolymers added were varied, and contents of other components were the same as in the actual example 34 described above and according to the procedure of the actual example 34. Results of the evaluation are shown in Table 11. Copolymers represented by the chemical formulae (30)~(34) were synthesized according to the method for synthesizing the copolymer having the chemical formula (29).

Formula (30)



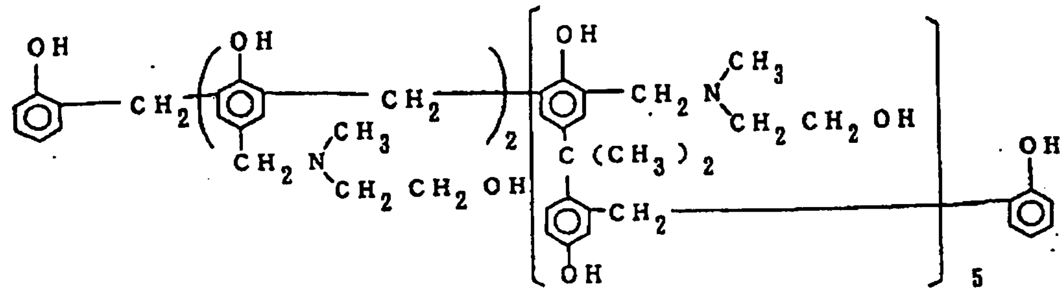
molar ratio of phenol/bisphenol = 2:6

Formula (31)



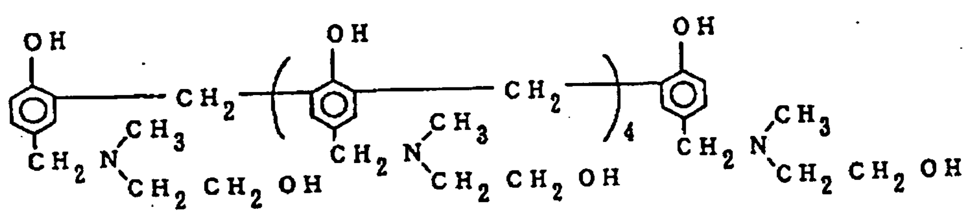
molar ratio of phenol/bisphenol = 7:2

Formula (32)

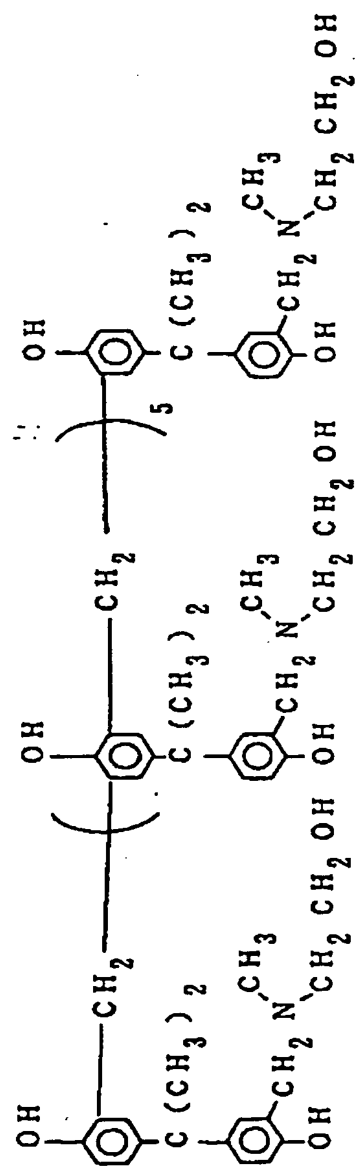


molar ratio of phenol/bisphenol = 4:5

Formula (33)



Formula (34)



Actual Example 38:

Shaped cans of Al-Mn series (JIS-A3004) were spray-degreased using an acidic degreasing agent (Surfcleaner NHC250, Nippon Paint Co., Ltd.) at a concentration of 30 g/l at 75°C for 60 seconds, and washed with water. Then, the

cans were subjected to a spray-conversion treatment at 50°C for 20 seconds with a metal surface treatment agent containing phosphoric acid (0.5 g/l), hydrofluoric acid (0.5 g/l), pyrophosphoric acid (0.5 g/l) and an amine-modified phenolic resin having the chemical formula (33) (0.6 g/l), an amine-modified bisphenolic A resin having the chemical formula (34) and adjusted to pH 3.5. Then, treated cans were washed with water, drained and dried at 190°C for 2 min. Results of the evaluation are shown in Table 12.

Actual Examples 39~41 and Comparative Examples 21~22:

Surface treatment was performed using metal surface treatment agents wherein contents of amine-modified phenolic and bisphenolic resins represented by chemical formulae (33) and (34), respectively, were varied, and contents of other components were the same as in the actual example 38 described above, and according to the procedure of the example 38. Results of the evaluation are shown in Table 12.

Table 12

		Resin composition in metal surface treatment agents		Evaluation item			
		Phenolic resin (33) (g/l)/bisphenolic resin (34) (g/l)	Molar ratio of phenolic resin/bisphenolic resin	Blackening resistance in boiling water	Sliding ability	Coating adhesiveness	Browning resistance
Actual example	38	0.6/0/.6	50/50	Excellent	Excellent	Excellent	Excellent
	39	1.0/0.2	83/17	Excellent	Excellent	Excellent	Excellent
	40	0.2/1.0	17/83	Excellent	Excellent	Excellent	Excellent
	41	0.1/0.1	50/50	Excellent	Excellent	Excellent	Excellent
Comparative example	21	1.2/0	100/0	Excellent	Excellent	Excellent	Poor
	22	0/1.2	0/100	Poor	Average	Excellent	Excellent

These results indicate that, using the agent and method of the metal surface treatment of the present invention, all examined characteristics, including corrosion resistance (blackening resistance in boiling water), sliding ability, and coating adhesiveness of metallic materials, were much improved as compared with those treated with the conventional agent and method.

In the following, preferred embodiments of the metal surface treatment agent containing organic high molecular compounds and other additives will be described.

Actual Examples 42~51 and Comparative Examples 23~25:

1. Objects to be treated

Cans fabricated by shaping an aluminum alloy plate of Al-Mn series (JIS-A3004) using DI techniques, etc.

2. Method for evaluating the undercoating film

a) Blackening resistance in boiling water (corrosion resistance)

The bottom portion of cans which had been surface-treated with the composition of the present actual and comparative examples were immersed in boiling water for 30 min, and their external appearance was evaluated in the following scale.

Excellent : No change in external appearance
Average : Slightly blackened
Poor : Blackened

b) Sliding ability of the undercoating film surface

The motion frictional coefficient of cans surface-treated by the method of the present actual example was determined using a Heidon-14 tester with 5 mmØ steel ball, a load of 50 g and a touching needle speed of 300 mm/min.

Excellent : Motion frictional coefficient less than 0.6.
Average : Motion frictional coefficient is 0.6~0.8.
Poor : Motion frictional coefficient greater than 0.8.

c) Coating adhesiveness

Surface-treated cans were pained with paint [base paint, BE-70-001N 150 mg/m^2; clear, EB-69-002N 60 mg/m^2 (BASF Co., Ltd.)] using a bar coater. Cans thus painted were subjected to wedge-bending, and an adhesive tape (Nichban cellotape) was stuck onto the bent portion, then peeled off. The peeling conditions were evaluated according to the following scale.

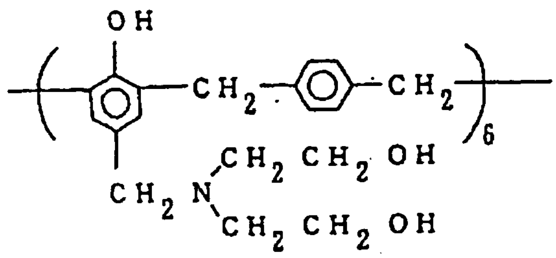
Excellent : Length of coating film peeled off with tape less than 15 mm.
Average : Length of coating film peeled off with tape 15~20 mm.
Poor : Length of coating film peeled off with tape greater than 20 mm.

3. Nitrogen atom-containing high molecular compounds

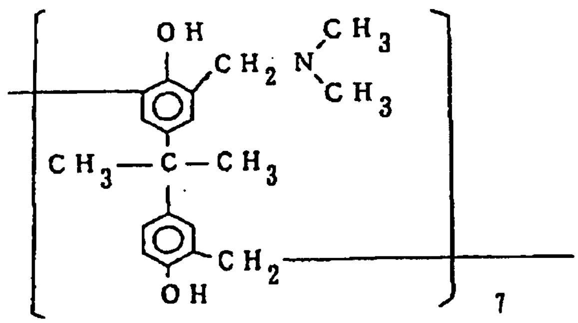
Acrylic resin (M):

HEA*1/p-TBS*2/DMAEA
Phenolic resin (N) : compound represented by the following chemical formula (35)
Phenolic resin (O) : compound represented by the following chemical formula (36)*3 = 40/30/30 Molecular weight 3,000

*1 : HEA hydroxyethyl acrylate
*2 : p-TBS para-t-butyl styrene
*3 : DMAEA N-dimethylaminoethyl acrylate



Formula (35)



Formula (36)

4. Conditions for metal surface treatment

Actual Example 42:

Shaped cans of Al-Mn series (JIS-A3004) were spray-degreased using an acidic degreasing agent (Surfcleaner NHC250, Nippon Paint, Co., Ltd.) at the concentration of 30 g/l at 75°C for 60 seconds, and washed with water. The cans were then subjected to a spray conversion treatment at 50°C for 20 seconds with a metal surface treatment agent containing phosphoric acid (0.5 g/l), hydrofluoric acid (0.5 g/l), a nitrogen atom containing acrylic resin (1.0 g/l) as the organic high molecular compound and hydrogen peroxide (0.5 g/l) as the oxidizing agent and adjusted to pH 3.5. Treated cans were washed with water, drained, and dried at 190°C for 2 min. Results of the evaluation are shown in Table 13.

Actual Examples 43~51 and Comparative Examples 23~25:

Surface treatment was performed using metal surface treatment agents wherein the species and content of organic high molecular compounds and oxidizing agents were changed with the pH value being altered, and contents of other components were the same as in the actual example 42 described above. Results of the evaluation are shown in Table 13.

Table 13

		Composition of metal surface treatment agent					Evaluation		
		Organic high molecular compound		Oxidizing agent		pH	Blackening resistance in boiling water	Sliding ability	Coating adhesiveness
		Species	Content (g/l)	Species	Content (g/l)				
Actual example	42	(M)	1.0	H_2O_2	0.5	3.5	Excellent	Excellent	Excellent
	43	(M)	1.0	$NaNO_3$	0.5	3.5	Excellent	Excellent	Excellent
	44	(M)	1.0	$NaClO_3$	0.5	3.5	Excellent	Excellent	Excellent
	45	(M)	1.0	$NaBrO_3$	0.5	3.5	Excellent	Excellent	Excellent
	46	(M)	1.0	H_2O_2	0.5	3.5	Excellent	Excellent	Excellent
	47	(M)	0.01	H_2O_2	0.5	3.5	Excellent	Excellent	Excellent
	48	(M)	1.0	H_2O_2	9.0	3.5	Excellent	Excellent	Excellent
	49	(M)	9.0	H_2O_2	0.02	3.5	Excellent	Excellent	Excellent
	50	(N)	1.0	H_2O_2	0.5	3.5	Excellent	Excellent	Excellent
	51	(O)	1.0	H_2O_2	0.5	3.5	Excellent	Excellent	Excellent
Comparative example	23	(M)	1.0	H_2O_2	0.005	3.5	Poor	Average	Excellent
	24	(M)	0.005	H_2O_2	0.5	3.5	Poor	Poor	Excellent
	25	(M)	15.0	H_2O_2	0.5	3.5	Excellent	Excellent	Average

These results indicate that, using the metal surface treatment agent of the present invention, all characteristics, including corrosion resistance (blackening resistance in boiling water), sliding ability, and coating adhesiveness, of metallic materials were improved as compared with those treated with the conventional agent.

Actual Examples 52~58 and Comparative Examples 26~27:

1. Objects to be treated

Cans fabricated by shaping an aluminum alloy plate of Al-Mn series (JIS-A3004) using DI techniques, etc.

2. Method for evaluating the undercoating film

a) Blackening resistance in boiling water (corrosion resistance)

Cans which had been surface-treated with the composition of the present actual and comparative examples were immersed in boiling water for 30min, and their external appearance was evaluated according to the following scale.

Excellent : No change in external appearance
Aerage : Slightly blackened

Poor : Blackened

b) Sliding ability of the undercoating film surface

The motion frictional coefficient of cans which had been subjected to the conversion treatment by the method of the present actual example was determined using a Heidon-14 tester with 5 mmØ steel ball, a load of 50 g and a touching needle speed of 300 mm/min.

Excellent : Motion frictional coefficient less than 0.55
Average : Motion frictional coefficient 0.55~0.8
Poor : Motion frictional coefficient greater than 0.8

c) Coating adhesiveness

Conversion-treated cans were painted with paint [EB-70-001N 150 mg/m^2; Clear, EB-69-002N 60 mg/m^2 (BASF Co.)] using a bar coater. Cans thus painted were subjected to wedge-bending, and an adhesive tape (Nichiban cello-tape) was suck onto the bent portion, then peeled off. The peeling conditions were evaluated according to the following scale.

Excellent : Length of coating film peeled off with tape less than 15 mm.
Average : Length of coating film peeled off with tape 15~20 mm.
Poor : Length of coating film peeled off with tape greater than 20 mm.

3. Conditions for metal surface treatment

Actual Example 52:

Shaped cans of Al-Mn series (JIS-A3004) were spray-degreased using an acidic degreasing agent (Surfcleaner NHC250, Nippon Paint, Co., Ltd.) at the concentration of 30 g/l at 75°Cfor 60 seconds, and washed with water. The cans were then subjected to spray conversion treatment at 50°C for 20 seconds with a metal surface treatment agent containing phosphoric acid (0.5 g/l), hydrofluoric acid (0.5 g/l), pyrophosphoric acid (0.5 g/l), aluminum ions and the following (P) as an organic high molecular compound and adjusted to pH 3.5. Then, the treated cans were washed with water, drained and dried at 190°C for 2 min. Results of the evaluation are shown in Table 14. Actual Example 52 ~ 58 and Comparative

Example 26 ~ 27:

Surface treatment was performed using metal surface treatment agents wherein the species and content of organic high molecular compounds, content of phosphoric ion, content of aluminum ion, changing with the pH value being altered, and content of other components were the same as in the actual example 52 described above. Results of the evaluation are shown in Table 14.

Table 14

		Composition of metal surface treatment agent					Evaluation		
		Organic high molecular compound		Phosphoric acid (g/l)	Al^{3+} (g/l)	pH	Blackening resistance in boiling water	Sliding ability	Coating adhesiveness
		Species	Content (g/l)						
Actual example	52	(P)	1.0	0.5	0.1	3.5	Excellent	Excellent	Excellent
	53	(P)	4.0	0.5	0.01	3.5	Excellent	Excellent	Excellent
	54	(P)	0.5	0.2	0.5	3.5	Excellent	Excellent	Excellent
	55	(P)	1.0	0.5	0.25	3.5	Excellent	Excellent	Excellent
	56	(Q)	1.0	0.5	0.1	3.5	Excellent	Excellent	Excellent
	57	(R)	1.0	0.5	0.1	3.5	Excellent	Excellent	Excellent
	58	(M)	1.0	0.5	0.1	3.5	Excellent	Excellent	Excellent
Comparative example	26	(P)	1.0	0.5	0	3.5	Poor	Average	Excellent
	27	(P)	1.0	0.5	1	3.5	Poor	Excellent	Excellent

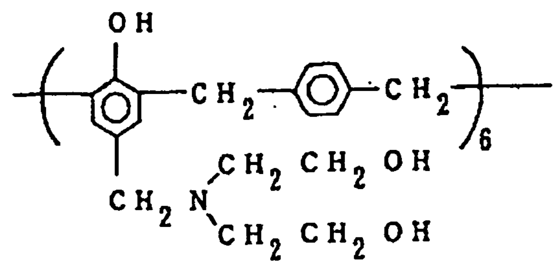
(P) : Phenolic resin, represented by the following chemical formula (37)

(Q): Polyvinylphenolic resin, represented by the following chemical formula (38)

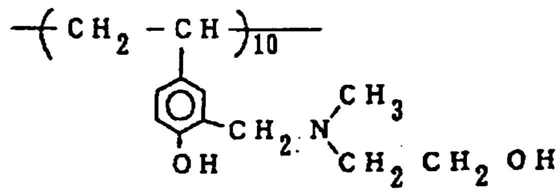
(R): Bisphenolic A resin, represented by the following chemical formula (39)

(M): Amine-modified cationic resin = acrylic resin (described above)

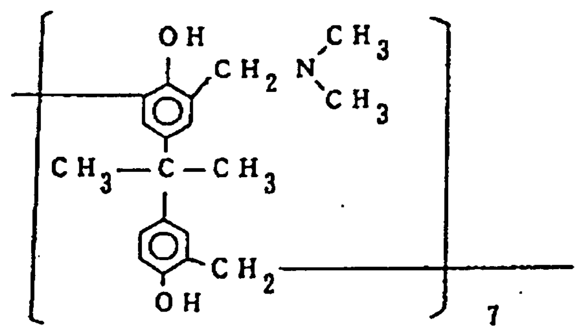
Formula (37)



Formula (38)



Formula (39)



These results clearly show that corrosion resistance (blackening resistance in boiling water), sliding ability, coating adhesiveness, and external appearance of objects treated with the metal surface treatment agent of the present invention are excellent even for treatment in presence of low concentrations of phosphoric acid.

Actual examples 59~70 and comparative examples 28~31:

1. Objects to be treated

Cans fabricated by shaping an aluminum alloy plate of Al-Mn series (JIS-A3004) using DI techniques, etc.

2. Method for evaluating the undercoating film

a) Blackening resistance in boiling water (corrosion resistance)

The bottom portion of cans which had been surface-treated with the composition of the present actual and comparative examples was immersed in boiling tap water for 30 min, and the external appearance was evaluated according to

the following scale.

Excellent : No change in external appearance
Average : Slightly blackened
Poor : Blackened

b) Sliding ability of the undercoating film surface

Motion frictional coefficient of cans which had been subjected to the conversion treatment was determined using a Heidon-14 tester with 5 mmØ steel ball a load of 50 g and a touching needle speed of 300 mm/min.

Excellent : Motion frictional coefficient less than 0.6
Average : Motion frictional coefficient 0.6~0.8
Poor : Motion frictional coefficient greater than 0.8

c) Coating adhesiveness

Surface-treated cans were painted with paint [EB-70-001N 150 mg/m^2; Clear, EB-69-002N 60 mg/m^2) (BASF Co.)] using a bar coater. Cans thus painted were subjected to wedge-bending, and an adhesive tape (Nichian cellotape) was stuck onto the bent portion, then peeled off. The peeling conditions were evaluated according to the following scale.

Excellent : Length of coating film peeled off with tape less than 15 mm
Average : Length of coating film peeled off with tape 15~20 mm.
Poor : Length of coating film peeled off with tape greater than 20 mm

3. Cationic nitrogen atom-containing resin

(P) : Phenolic resin represented by the chemical formula (37) described above
(Q) : Polyvinylphenolic resin represented by the chemical formula (38) described above
(R) : Bisphenol A resin represented by the chemical formula (39) described above
(M) : Amino-modified cationic resin described above

4. Conditions for metal surface treatment

Actual Example 59:

Shaped cans of Al-Mn series (JIS-A3004) were spray-degreased using an acidic degreasing agent (Surfcleaner NHC250, Nippon Paint, Co., Ltd.) at a concentration of 30 g/l at 75°C for 60 seconds, and then washed with water. The cans were then subjected to a spray conversion treatment at 50°C for 20 seconds with a metal surface treatment agent containing phosphoric acid (0.5 g/l), hydrofluoric acid (0.5 g/l), a cationic nitrogen atom-containing acrylic resin (1 g/l) as the organic high molecular compound, and molybdic acid ion (0.02 g/l) as the polyvalent anion and adjusted to pH 3.5. The treated cans were then washed with water, drained and dried at 190°C for 2 min. Results of the evaluation are shown in Table 15.

Actual Examples 60~70 and Comparative Examples 28~31:

As shown in Table 15, surface treatment was performed using metal surface treatment agents wherein species and contents of the organic high molecular compounds described above as well as polyvalent anions were varied under different pHs, and contents of other components were the same as in the actual example 59 described above and according to the procedure of the actual example 59 described above. Results of the evaluation are shown in Table 15.

Table 15

		Composition of metal surface treatment agent					Evaluation item		
		Organic high molecular compound		Polyvalent anion		pH	Blackening resistance in boiling water	Sliding ability	Coating adhesiveness
		Species	Content (g/l)	Species	(g/l)				
Actual example	59	(P)	1.0	Molybdic acid	0.02	3.5	Excellent	Excellent	Excellent
	60	(P)	1.0	Tungstic acid	0.05	3.5	Excellent	Excellent	Excellent
	61	(P)	0.1	Tungstic acid	5	3	Excellent	Excellent	Excellent
	62	(P)	5.0	Tungstic acid	0.1	4	Excellent	Excellent	Excellent
	63	(P)	10.0	Phosphomolybdic acid	0.01	3.5	Excellent	Excellent	Excellent
	64	(P)	1.0	Phosphotungstic acid	0.05	3.5	Excellent	Excellent	Excellent
	65	(P)	2.0	Silicotungstic acid	0.03	3.5	Excellent	Excellent	Excellent
	66	(P)	0.01	Silicotungstic acid	5	3.5	Excellent	Excellent	Excellent
	67	(P)	1.0	Vanadic acid	0.5	3.5	Excellent	Excellent	Excellent
	68	(Q)	1.0	Molybdic acid	0.05	3.5	Excellent	Excellent	Excellent
	69	(R)	1.0	Molybdic acid	0.05	3.5	Excellent	Excellent	Excellent
	70	(M)	1.0	Molybdic acid	0.05	3.5	Excellent	Excellent	Excellent
Comparative example	28	(P)	1.0	-	-	3.5	Poor	Average	Excellent
	29	(P)	0.005	Molybdic acid	0.05	3.5	Poor	Poor	Average
	30	(P)	15.0	Molybdic acid	0.05	3.5	Excellent	Excellent	Average
	31	(P)	1.0	Tungstic acid	15	3.5	Poor	Poor	Average

These results clearly have shown that not only corrosion resistance (blackening resistance in boiling water), but also sliding ability as well as coating adhesiveness of objects treated with the metal surface treatment agent of the present invention are all improved as compared with those treated with the conventional agent.

Possible industrial applications

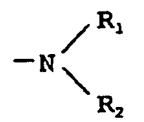
Metal surface treatment agents and methods in accordance with the present invention are applicable for the sur-

face treatment of food cans, automobile bodies, steel plate coil coating, building materials, etc.

Claims

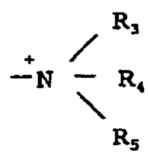
1. A metal surface treatment agent comprising a water-soluble, water-dispersive, or emulsive organic high molecular compound or its salt which contains more than one nitrogen atom represented by the following formula [a] or cationic sulfur atom.

[a]:



(where R_1 and R_2 = H, OH or $C_{1\sim10}$ straight or branched chain alkyl groups with possible substitutions, or $C_{1\sim10}$ straight or branched chain alkanol groups with possible substitutions)

or



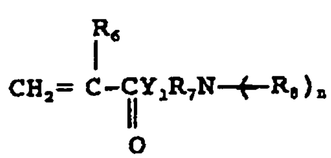
(where R_3, R_4 and R_5 = H, OH or $C_{1\sim10}$ straight or branched chain alkyl groups with possible substitutions, or $C_{1\sim10}$ straight or branched chain alkanol groups with possible substitutions)

2. The metal surface treatment agent according to Claim 1 wherein said organic high molecular compound or its salt is any one resin chosen from the group including epoxy resin, acrylic resin, urethane resin, phenolic resin, polybutadiene resin, polyamide resin, and olefin resin.

3. The metal surface treatment agent according to Claim 1 wherein said organic high molecular compound or its salt having more than one of said nitrogen atom contains 1~5 phenolic groups, 1~5 hydroxyl groups, and 1~10 nitrogen atoms per 500 molecular weight.

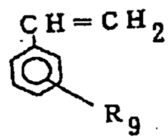
4. The metal surface treatment agent according to Claim 1 wherein said organic high molecular compound or its salt having more than one of said cationic sulfur atom contains 1~5 phenolic groups, 1~12 hydroxyl groups, and 0.1~7 cationic sulfur atoms per 500 molecular weight.

5. The metal surface treatment agent according to Claim 2 wherein said organic high molecular compound is an acrylic resin where said acrylic resin is a copolymer comprising monomers represented by the following structural formulae [b], [c], and [d].



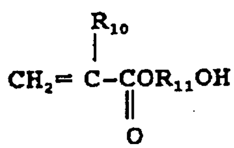
[b]

(where R_6 = H or methyl group,
R_7 = $C_{1\sim5}$ alkylene group,
R_8 = $C_{1\sim5}$ alkyl group,
Y_1 = -NH- or -O-,
n = 2 or 3)



[c]

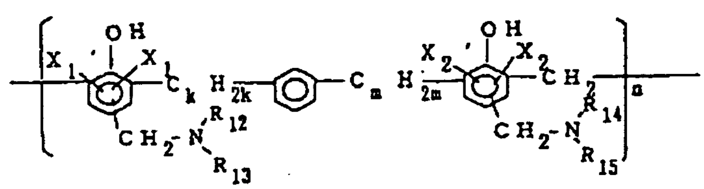
(where R_9 = methyl, ethyl, butyl, or *tert*-butyl groups)



[d]

(where R_{10} = H or methyl group,
R_{11} = $C_{1\sim5}$ alkylene group)

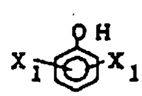
6. The metal surface treatment agent according to Claim 2 wherein said organic high molecular compound is a phenolic resin comprising the repeating unit represented by the following formula [e].



[e]

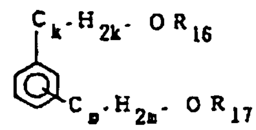
(where R_{12}, R_{13}, R_{14} and R_{15} = H, $C_{1\sim5}$ alkyl or alkanol groups with or without substitutions,
X_1, X_1', X_2 and X_2' = H, OH or $C_{1\sim5}$ alkyl groups with or without substitution
k and m = 15, n = 13)

7. The metal surface treatment agent according to Claim 2 wherein said organic high molecular compound is a phenolic resin and said phenolic resin is a polycondensation product or its salt comprising a phenolic compound monomer having the following structure [f], dialkylbenzene glycol monomer having the following structure [g], formaldehyde, and an amine having the following structure [h].



[f]

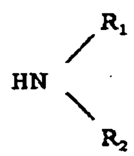
(where X_1, X_1', X_2 and X_2' = H, OH or $C_{1\sim5}$ alkyl groups with or without substitution)



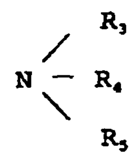
[g]

(where R_{16} and R_{17} = H, OH or $C_{1\sim5}$ alkyl groups with or without substitution K' and m' = 1~5)

[h]:



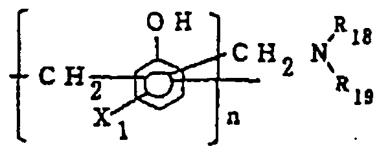
or



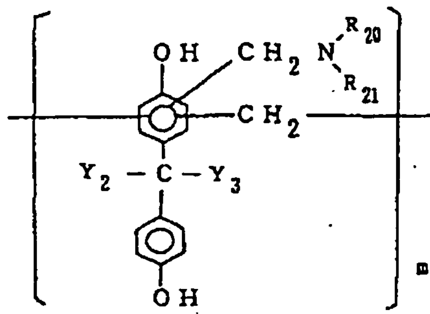
(where R_1~R_5 = H, OH or $C_{1\sim10}$ straight or branched chain alkyl groups with possible substitutions, or $C_{1\sim10}$ straight or branched chain alkanol groups with possible substitutions)

8. The metal surface treatment agent according to Claim 2 wherein said organic high molecular compound is a phenolic resin obtained by reacting a phenolic condensation product prepared by reacting, in the presence of organic or inorganic acids as the catalyst, lrnol of a phenolic compound monomer represented by the formula [f] described above, 0.02~0.6 mol of dialkylbenzene glycol monomer represented by the formula [g] described above, of and formaldehyde, the amount which is adjusted so that the sum of amounts of formaldehyde, and dialkylbenzene glycol monomer represented by the formula [g] described above to be 0.7~0.9 mol, with 0.5~2.0 mol of an amine represented by the formula h described above and the equimolar amount of formaldehyde as that of said amine.

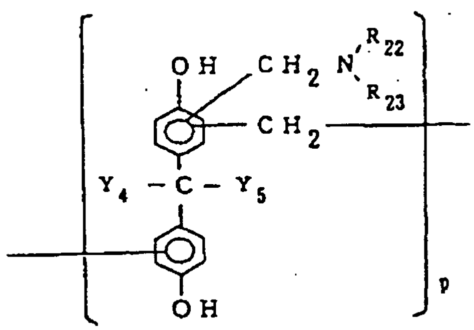
9. The metal surface treatment agent according to Claim 2 wherein said organic high molecular compound is a phenolic resin which comprises a repeating phenolic unit represented by the following formula [i] and other repeating bisphenolic unit represented by the following formulae [j] and/or [k], with the weight ratio of [i]: [j] and/or [k] being 90:10~10:90, and contained in said metal surface treatment agent at the concentration of 0.01~10 g/l.



[i]



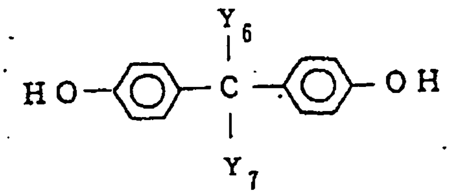
[j]



[k]

(where R_{18}, R_{19}, R_{20}, R_{21}, R_{22}, R_{23}, Y_2, Y_3, Y_4 and Y_5 = H, OH, $C_{1\sim10}$ straight or branched chain alkyl groups, or $C_{1\sim10}$ straight or branched chain alkanol groups, and m, n and p are 2~50, respectively. These alkyl or alkanol groups may be substituted with functional groups.)

10. The metal surface treatment agent according to Claim 2 wherein said organic high molecular compound is a phenolic resin which is a phenol-bisphenol-formaldehyde polycondensation product or its salt which is a condensation product composed of a phenolic compound having the structure [f] described above, a bisphenolic compound having the structure [l] shown below and formaldehyde, and linked to at least one amine having the structure [h] described above, where the molar ratio of said phenolic compound [f] and said bisphenolic compound [l] in said phenol-bisphenol-formaldehyde polycondensation product or its salt is 9:1~1:9, and contained in the metal surface treatment agent at the concentration of 0.01~10 g/l.



[1]

(where Y_6 and Y_7 = H, OH or $C_{1\sim10}$ straight or branched chain alkyl groups, or $C_{1\sim10}$ straight or branched alkanol groups. These alkyl or alkanol groups may be substituted with functional groups.)

11. The metal surface treatment agent according to any one of Claims 1 to 10 further comprising heavy metal or its fluoride, nitrate, and phosphate.

12. The metal surface treatment agent according to any one of Claims 1 to 10 further comprising an oxidising agent, and wherein said metal surface treatment agent contains said organic high molecular compound at 0.01~10 g/l and said oxidising agent at 0.01~10 g/l.

13. The metal surface treatment agent according to Claim 12 further comprising inorganic acid at 0.01~10 g/l.

14. The metal surface treatment agent according to Claim 13 further comprising heavy metal at 10 g/l.

15. The metal surface treatment agent according to Claims 11 or 14 wherein said heavy metal is one or more of those belonging to the group including zirconium, molybdenum, tungsten, niobium, nickel, cobalt, manganese, and tantalum.

16. The metal surface treatment agent according to Claim 12 wherein said oxidizing agent is any one of those including hydrogen peroxide, nitrous acid, nitrite, perboric acid, chloric acid, chlorate, bromic acid, and bromate.

17. The metal surface treatment agent according to any one of Claims 1 to 10 further comprising phosphate ions and aluminum ions, and wherein said metal surface treatment agent comprises said organic high molecular compound at 0.01~10 g/l, said phosphate ions at 0.01~0.8 g/l, and said aluminum ions at 0. 01~0.5 g/l.

18. The metal surface treatment agent according to any one of Claims 1 to 10 further comprising polyvalent anions wherein said metal surface treatment agent comprises said organic high molecular compound at 0.01~10 g/l and said polyvalent anions at 0.03~10 g/l.

19. The metal surface treatment agent according to Claim 18 wherein said polyvalent anion is one or more of those belonging to the group including molybdenic acid, tungstic acid, vanadic acid, phosphomolybdenic acid, phosphotungstic acid, and silicotungstic acid, and their salts.

20. A metal surface treatment method wherein said method comprises the contact treatment of a metal surface with the metal surface treatment agent according to any one of Claims 1 to 19, successive washing with water, and drying.

21. A metallic material treated with the metal surface treatment agent according to any one of Claims 1 to 19.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP96/01902

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl[6] C23C22/00, C23C30/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl[6] C23C22/00-C23C22/86, C23C30/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922 - 1996
Kokai Jitsuyo Shinan Koho	1971 - 1996
Toroku Jitsuyo Shinan Koho	1994 - 1996

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	JP, 6-316771, A (NKK Corp., Mitsui Toatsu Chemicals, Inc., Kansai Paint Co., Ltd.), November 15, 1994 (15. 11. 94),	
X	Claims 1, 2, 5; column 5, line 25 to column 6, line 31, column 8, line 35 to column 9, line 1, column 12, line 11 to column 13, line 5	1, 2, 11-21
Y	Column 5, line 25 to column 11, line 10 (Family: none)	3 - 10
	JP, 5-186737, A (Mitsubishi Petrochemical Co., Ltd.), July 27, 1993 (27. 07. 93),	
X	Claims 1 to 6, column 3, line 44 to column 6, line 10	1, 2, 11, 15, 16, 20, 21
Y	Column 3, line 44 to column 6, line 10 (Family: none)	3, 4, 6-10, 12-14
	JP, 5-247381, A (Nissan Chemical Industries, Ltd.), September 24, 1993 (24. 09. 93),	
X	Claim 1; column 2, line 22 to column 4, line 41	1, 2, 20, 21

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
September 27, 1996 (27. 09. 96)	October 8, 1996 (08. 10. 96)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP96/01902

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Claim 1; column 2, line 22 to column 4, line 41 (Family: none)	3, 4, 6-10
	JP, 1-177379, A (Kao Corp.), July 13, 1989 (13. 07. 89),	
X	Claims 1 to 6; page 3, upper right column, line 16 to page 6, lower right column, line 1	1, 2, 20, 21
Y	Claims 1 to 6; page 3, upper right column, line 16 to page 6, lower right column, line 1 & JP, 1-177380, A & JP, 1-177381, A & US, 4978399, A & US, 5246507, A	1, 4, 6-10
	JP, 53-41325, A (Hodogaya Chemical Co., Ltd.), April 14, 1978 (14. 04. 78),	
X	Claim 1 (Family: none)	1
	JP, 49-113735, A (Ordena Trudovogo Krasnogo Znameni Institut Himii Himitesukoi Ciewnology Akademii Nauk Ritofuskoi SSR), October 30, 1974 (30. 10. 74),	
X	Claim 1 (Family: none)	1, 11-60, 20, 21
	JP, 2-43376, A (Sumitomo Metal Industries, Ltd.), February 13, 1990 (13. 02. 90),	
Y	Claims 1, 2; page 3, lower right column, line 19 to page 4, lower right column, line 14	1, 20, 21
Y	Claims 1, 2; page 3, lower right column, line 19 to page 4, lower right column, line 14 (Family: none)	11 - 16
	JP, 57-501289, W (Henkel KGaA.), July 22, 1982 (22. 07. 82),	
X	Claims 1 to 18	1, 20, 21
Y	Claims 1 to 18 & WO, 8200665, A & EP, 58711, A	11 - 18
	JP, 8-25553, A (Sumitomo Metal Industries, Ltd.), January 30, 1996 (30. 01. 96),	
P	Claim 1; column 3, line 15 to column 6, line 4 (Family: none)	1, 11-13, 20, 21
	JP, 3-31484, A (Nihon Parkerizing Co., ltd.), February 12, 1991 (12. 02. 91),	
A	Claims 1, 2 & EP, 405340, A & US, 5091223, A	1, 11-21
	JP, 2-43375, A (Sumitomo Metal Industries, Ltd.), February 13, 1990 (13. 02. 90),	
A	Claims 1 to 4; page 4, upper left column, line 7 to lower right column, line 10	1, 10-21

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP96/01902

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	(Family: none)	
A	JP, 49-59050, A (Noranda Mines Ltd.), June 7, 1974 (07. 06. 74), Claims 1 to 21 & DE, 2342256, A & US, 4093780, A & CA, 1006074, A & GB, 1397365, A	1, 11-21

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